METHOD OF ENHANCING THE SENSITIVENESS OF ALKALI METAL PHOTOELECTRIC CELLS

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Abstract

A technique is described for sensitizing alkali metal photoelectric cells to light by introducing onto the metal surface small amounts of dielectrics, as oxygen, water vapor, sulphur vapor, sulphur dioxide, hydrogen sulphide, air, sodium bisulphite, carbon bisulphide, etc., or some organic compound as methyl alcohol, acetic acid, benzene, nitrobenzene, acetone, etc., or some organic dye as tropaeolin, rosaniline base, eosin, cyanine, kryptocyanine, dicyanine, neocyanine, etc. The marked increase in electron emission from the cathodes of cells so treated is due primarily to an increase in response to red and infrared light. Vacuum sodium cells have been produced, yielding photoelectric currents as high as 7 microamperes per lumen of white light of color temperature 2848°K and caesium cells yielding far greater currents.

The response of these cells is proportional to the intensity of the exciting light even for light of longer wave-lengths than that to which the cell responded before treatment.

Spectral response curves are similar for all cells using the same metal as cathode. These curves differ from the curves for the pure metal by the appearance of a new selective maximum at lower frequencies. This newly appearing maximum resembles the regular maximum for the untreated metal and is always separated from it by the frequency of a well-known line in the vibration-rotation spectrum of the dielectric molecules, usually the 1.5μ line so characteristic of oxygen-hydrogen, carbon-hydrogen or nitrogen-hydrogen linkages. The long wave limit shifts an amount agreeing with the separation of the maxima.

With a cell so designed that the cathode could be sensitized in a side chamber and then slipped into its proper place (thus keeping the anode free from light-sensitive materials), stopping potentials were obtained for electrons, liberated by monochromatic light, from a sodium cathode before and after treating it with sulphur vapor and air. For light of wave-lengths ranging from λ3500A to λ8000A falling on the treated cathode, the electron retarding potentials are found to vary linearly with the frequency of the exciting light, thus establishing the validity of Einstein's photoelectric equation for composite surfaces. From the slope of the straight line depicting this relationship, the value of Planck's constant h is found to be 6.541×10^{-27}, significant to three figures. An almost identical value is obtained for untreated sodium. The apparent stopping potentials, or voltages at which the photoelectric currents become zero are the same before and after the sulphur and air treatment. The voltage at which the current just saturates is always greater after treatment than before. This is a measure of the change in contact potential of the cathode due to the presence of the sulphur and air. Changes of approximately 0.8 volts are common.

The validity of Einstein's equation precludes the possibility of explaining the new maximum in the spectral response curve for a treated surface by a "Raman shift" of the incident light frequencies, even though the separation of these maxima is equal to certain well-known vibration-rotation frequencies of the dielectric molecules. It may be that the natural frequency of the alkali metal atom is diminished by the vibration frequency of the complex atom in which it is incorporated.

The Lindemann formula for the frequency of the selective photoelectric maximum $[2\pi\nu = (ne^2/mr^3)^{1/2}]$, primitive though it seems in the light of modern theory, has always given values for the pure metals in close agreement with experimental determinations. The n term is determined by the valence of the substance, a choice of unity being used for the monovalent alkali metals corresponding to an electron revolving around a singly charged ion. A choice of 2, 3,—for divalent, trivalent,—substances corresponds to electrons revolving around doubly, triply—charged ions. Under certain conditions the alkali metals manifest different valencies, such for instance, as those exhibited in the oxide series Na_2O_2, Na_2O, Na_3O, Na_4O. These compounds can be prepared in vacuum and are light-sensitive. Spectral response curves for such cells exhibit all the selective maxima called for by the Lindemann formula when the value of n is chosen to agree with the valence of the metal. Data are presented showing this condition to be general for the alkali metals, a maximum response to red or infrared light being dependent upon the formation of a subvalent compound, as a suboxide.

Attention is called to seemingly analogous phenomena in the fields of photoelectricity, photography, fluorescence and absorption.

THE work which culminated in the results to be reported in this paper was inspired by the simple inference that, since photoelectric emission from potassium is greatly increased by a non-conducting hydride film on the surface,[1,2] some other dielectric film might be still more effective in the same sense. As will be seen the consequences were far-reaching. Not only have far more sensitive photoelectric cells been developed but their characteristics have been studied sufficiently to throw some light on the cause of the increase. Moreover, the results of the rather extensive research suggest plausible explanations of various phenomena in the fields of absorption, photoelectricity, fluorescence and photography.

A. APPARATUS FOR MEASURING PHOTOELECTRIC CURRENTS

The response of photoelectric cells to unresolved light was always measured on a high sensitivity Leeds and Northrup galvanometer, a system of external shunts being used to lower the sensitivity as the magnitude of the photoelectric currents increased. Currents as small as 10^{-10} amperes could be conveniently determined in this way with the instrument on which the largest currents obtainable were measured.

The photoelectron emissions for highly resolved light, represented by the ordinates of the spectral response curves which follow, were measured by a Compton quadrant electrometer using a resistance leak of the order of 10^4 megohms. By suitably adjusting the needle voltage, steady deflections were easily readable for currents as small as 10^{-14} amperes.

The source of light was usually a glowing tungsten filament of horizontal candle power about 70 and color temperature 2848°K. To resolve or disperse this light, a high precision Hilger monochromator was used. Proper corrections for the dispersion of the prism were made. All data plotted in the spectral response curves of this paper represent current per unit energy of the incident light, unless otherwise specified.

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[1] Elster and Geitel, Phys. Zeits. **11,** 257 (1910).

[2] K. Moers, Zeit. Anorg. Chem. **113,** 179 (1920).

The ordinate values for any one figure are not directly comparable with those of any other.

B. Sensitization of Cells with Vapors from Sulphur

1. *Potassium surfaces.* The first experiment with dielectric films on light sensitive cathodes was performed by admitting sulphur vapor to a potassium surface in vacuum. The technique involved in the manufacture of these cells is given here as typical of that for all the cells made and used throughout the series of tests herein reported, except where otherwise specified.

A glass bulb of the shape shown in Fig. 1. was connected to a vacuum pump by means of a distilling tube, in a side chamber of which was a slug of previously distilled potassium. In the center of the cells was a metallic ring *A* with a wire leading through the glass walls to form an anode. A lead-in wire came through the bottom of the cell to make contact with the potassium when it was deposited on the glass walls. A small glass tube *D* containing ordinary commercial flowers of sulphur was sealed onto the stem of the bulb. The U-shaped section *C* of this tube could be immersed in liquid air to trap the vapors coming from the sulphur.

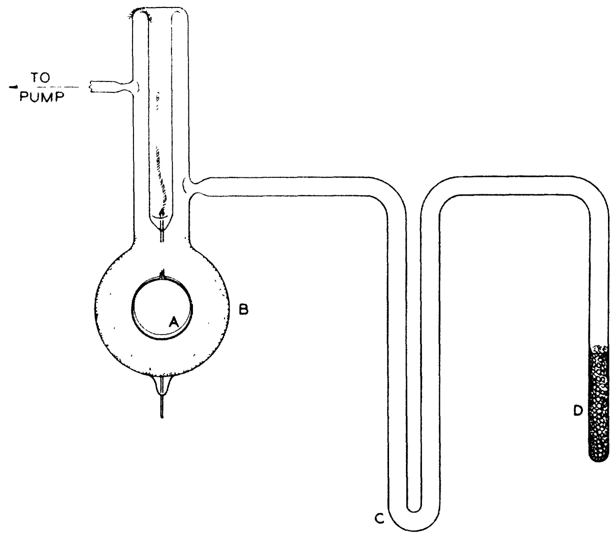

Fig. 1. Experimental type photoelectric cell. *A*-Ring-shaped anode. *B*-Bulb coated on inside with alkali metal to form cathode. *C*-Liquid air trap. *D*-Side arm containing dielectric.

After thorough evacuation of the system, the potassium in the distilling tube was melted and then distilled against the suction of the pump into the glass bulb and a coating made on the inner walls *B*. With a point flame a clear space about one inch in diameter for admitting the exciting light was made on the side of the bulb. As the light fell on the potassium surface, a galvanometer in series with the cell showed that a steady, though limited, emission of electrons was going on. The side tube containing sulphur was then heated and a very small amount sublimed onto the potassium coating.

The pump was left running during this treatment. The galvanometer registered an increased emission of electrons almost immediately and this continued until a certain critical amount of sulphur vapor had come in contact with the surface after which the number of electrons liberated by the light, began rapidly to decrease.

Table I gives a typical history of the treatment of a potassium surface with sulphur vapor, showing the relative current values for two different polarizing voltages at every stage in the process.

TABLE I.

Cathode History	P.E. Current at Cathode Voltages −8	 −50
Freshly distilled potassium	34.	38.
After admitting a trace of sulphur vapor	179.	217.
After admitting more sulphur vapor	905.	424.
Incident light diffused by ground glass	542.	542.
Slightly more sulphur admitted	840.	386.
Sulphur tube sealed off	846.	418.
Very low pressure of Argon	1360.	2280.
Argon pressure increased to 0.1 mm	1470.	4120.

It was noted that once the dielectric film began to build up, as shown by a change in the surface color, the current values were larger at low voltages than at high. This has been quite generally observed with this type cell, the voltage-current curves showing a maximum sometimes at cathode voltages as low as −5 volts. This maximum disappeared with the introduction of argon into the cell, and a general increase in measurable current even at low voltages was noted. A typical series of voltage current curves for a potassium surface treated with sulphur vapor is shown in Fig. 2. Another series for a rubidium cell similarly treated is reproduced in Fig. 3. The irregularities exhibited in these curves could be smoothed out by focusing the incident light on the side of the cell rather than the back, or by passing it through a diffusing glass. This suggested that they were due to the shape or design of the tube, an interesting observation which will be further discussed in a later section of this paper.

TABLE II.

Color of exciting light	EK filter used	KSH cell	KS cell	KH cell
White	None	374	374	374
Violet	#76	11	11	20
Blue	#78	93	101	132
Green	#60	59	85	44
Yellow	#16	120	72	9
Red	#29	58	11	1

It developed early in the work that the photoelectric emissions from potassium surfaces treated as described above were not only greater than those of potassium hydride cells for unresolved light, but the response to red light was decidedly larger. Even more striking results of this character were obtained in some cases by flashing hydrogen on the surface treated with sulphur. Table II illustrates the relative sensitivities to colored light on a scale in which the emissions under the action of total light are made equal. The letters used to describe the cells refer to the elements known to be present at the cathode surface.

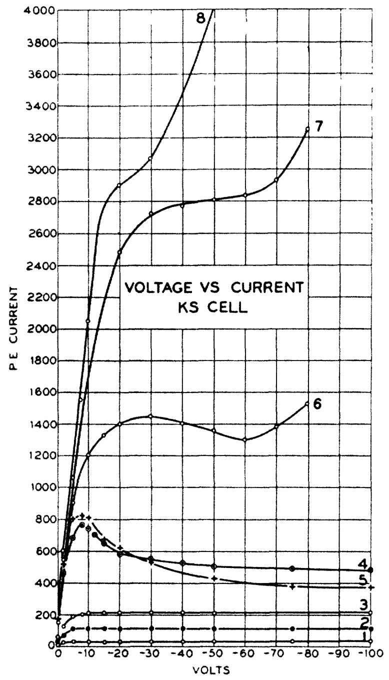

Fig. 2.

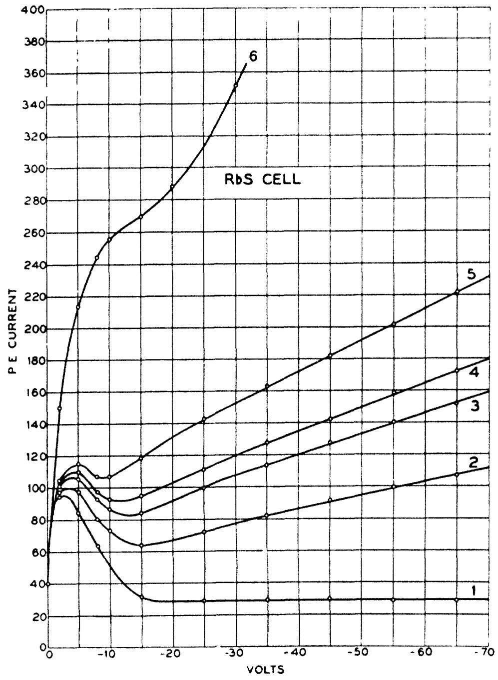

Fig. 3.

Fig. 2. Voltage-current curves for different stages in the manufacture of a potassium-sulphur vapor photoelectric cell. 1—For pure potassium cathode. 2–5—After successive treatments with sulphur vapor. 6–8—After successive admission of increasing pressures of argon.

Fig. 3. Voltage-current curves for a rubidium-sulphur vapor photoelectric cell containing different pressures of argon. 1 Vacuum condition. 2–6 Argon pressure gradually increased.

The color temperature of the constant light source used in the preparation of this table was not known, but Fig. 4 shows the relative sensitivities of KH and KS cells to white light of color temperature 2848°K. The new cells were very stable and showed little change in emission upon aging, the tendency being rather frequently to increase slightly in sensitivity during the first few days after sealing off the pump. In Fig. 5 are plotted some curves showing relative sensitivities throughout the spectrum. These curves, taken with spectrally resolved light, are corrected so that the ordinates, representing current per unit of light energy incident on the surface, are equal at the selective maxima.

It will be noted that the large selective maximum for each of these curves lies in the blue-violet region of the spectrum but that the maximum for the potassium-sulphur cell is slightly displaced toward shorter wave-lengths. The long wave end of the curves for this cell can be represented as an amplified sensitivity curve for pure potassium plus an additional curve representing a new maximum symmetrically drawn about 6200A. This maximum could be greatly enhanced by proper treatment and its importance should not be overlooked. It falls in that portion of the spectrum where the energy content of radiations from most illuminating systems is large, and its presence figured strongly in increasing the response of a cell to white light. Further discussion of this part of the curve will be reserved for a subsequent section of this paper.

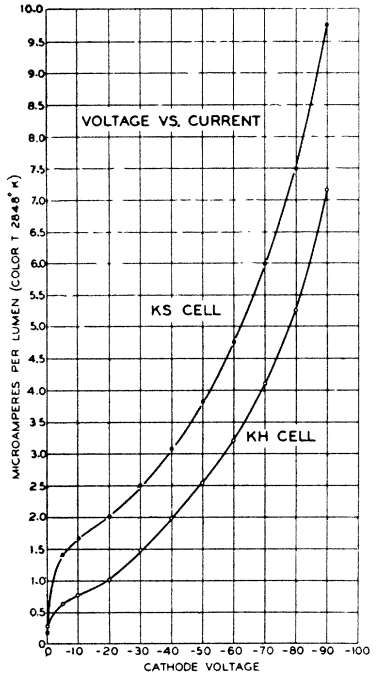

Fig. 4.

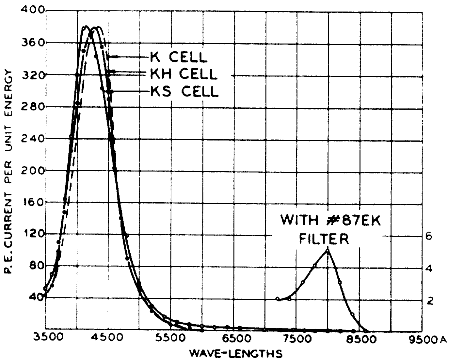

Fig. 5.

Fig. 4. Relative sensitivities of potassium-sulphur vapor and potassium-hydride photoelectric cells.

Fig. 5. Spectral response curves for potassium, potassium-hydride and potassium-sulphur vapor photoelectric cells.

2. *Rubidium and caesium surfaces.* Encouraged by the increase in response to red light manifested by potassium cells treated with sulphur vapor, the same treatment was applied to rubidium and caesium. Since the selective maxima[3] and the long wave limits[4] for these two alkali metals are or-

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[3] F. Gross, Zeits. f. Physik **7**, 316 (1921).

[4] B. Gudden, "Lichtelektrische Erscheinungen" p. 40 Julius Springer, Berlin (1928).

dinarily found at greater wave-lengths than for potassium, it was thought that surfaces of these metals, treated as above, should yield electrons more freely than potassium when excited by red or infrared light. However, disappointment in this respect attended all early efforts, presumably because the low melting points and high vapor pressures of rubidium and caesium would not permit the formation of a definite surface structure. The results illustrated for a treated caesium film in Fig. 6, differ only from what would be expected with a pure caesium film by the presence of a maximum between 5000A and 5500A. This is the wave-length region at which caesium in bulk form has been observed to manifest a selective maximum.[5]

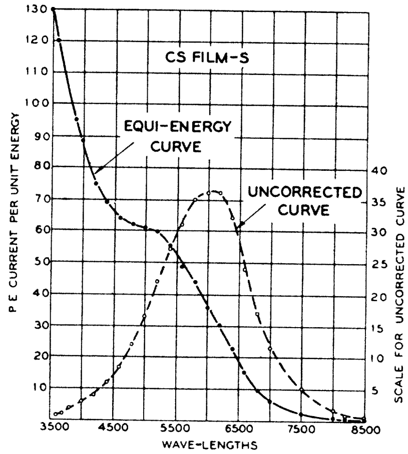

Fig. 6.

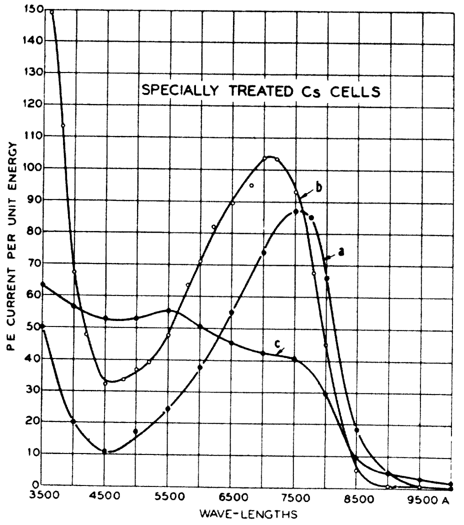

Fig. 7.

Fig. 6. Spectral distribution of sensitivity for a caesium film on magnesium plus sulphur vapor.

Fig. 7. Spectral distribution of sensitivity for a specially treated caesium photoelectric cell. Curves (a) and (b) were obtained from cells treated to give maximum response to red light. Curve (c) was obtained on a similar cell having less red sensitivity.

Early difficulties in treating caesium surfaces effectively with gases have in great measure been overcome by subsequent development of a technique for controlling the amounts of the various constituents which make up the cathode, so as to form the proper compounds. The rather remarkable results obtained with these cells supplement the data contained in this paper and will constitute the subject of a later publication. Suffice it to say that the photoelectric yield for properly treated caesium cathodes is almost entirely due to a marked response to deep red and infrared light, as shown in Fig. 7.

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[5] E. F. Seiler, Astrophys. J. **52,** 3, 129 (1920).

3. *Sodium surfaces.* The difficulties which arose in connection with the manufacture of rubidium and caesium cells suggested the advisability of using sodium as the photosensitive material. It was found in fact that when sodium was treated similarly with sulphur vapor, photoelectric cells were evolved having much greater sensitivity than the potassium-sulphur cells previously described. Moreover, the cause of this was found to be increased response to light at the long wave end of the visible spectrum and in the infrared.

Fig. 8 shows a typical curve giving photoelectric current per unit of exciting light energy for such a cell throughout the spectrum. The maximum at λ3600A should probably appear at a slightly shorter wave-length as it is likely that some absorption of the incident light by the glass walls of the cell occurs below λ3800 or 4000A. However, the fact that Richardson and Compton[6] found this maximum at λ3600A, and Pohl and Pringsheim[7] at λ3400A shows that the peak had not been shifted appreciably by the treatment with sulphur vapor. It was the appearance of a new maximum at approximately λ4800A that was most significant. In Fig. 9 are found three curves comparing the spectral response of a sodium-sulphur cell with that of two types of potassium cell.

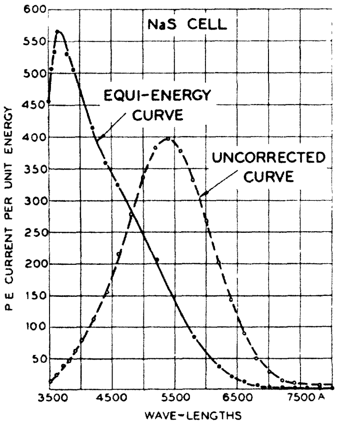


Fig. 8.

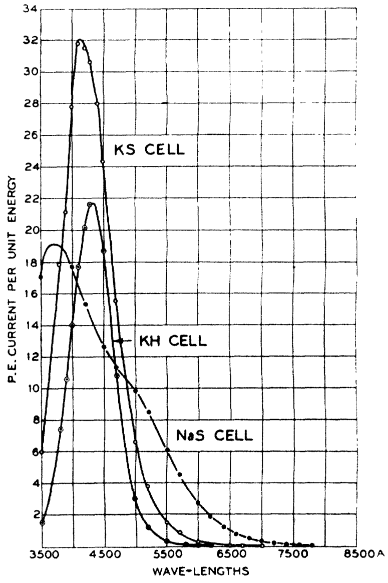


Fig. 9.

Fig. 8. Spectral response curve for a sodium-sulphur vapor cell. The broken curve is a plot of actual electrometer readings.

Fig. 9. Relative sensitivity of potassium hydride, potassium-sulphur vapor and sodium-sulphur cells throughout the spectrum.

[6] O. W. Richardson and K. T. Compton, Phil. Mag. **26**, 549 (1913).

[7] R. Pohl and P. Pringsheim, Verh. d. D. Phys. Ges. **14**, 46 (1912).

By applying a point flame momentarily near the edge of the cell window and temporarily producing a vapor of the sodium and the gas occluded on it, a startling increase in sensitivity was brought about. The response of the surface to white light of color temperature 2848°K after this last treatment was about double that observed before. Moreover, the increase was again chiefly in the red and infrared regions, as shown in Fig. 10. The new spectral emissivity curve could be broken up into a regular curve for sodium greatly amplified plus a new curve with a pronounced maximum at approximately λ4800A. In Fig. 11 is found a record of the spectral distribution of emissions for each step in the sensitizing process.

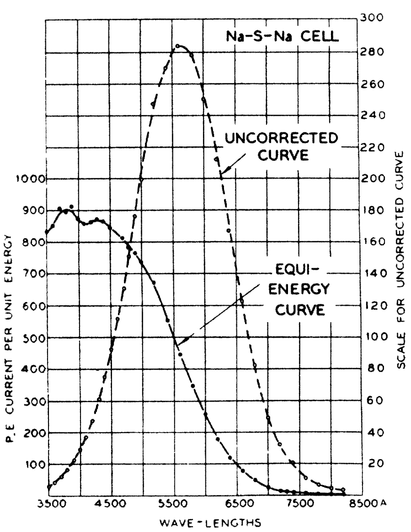


Fig. 10.

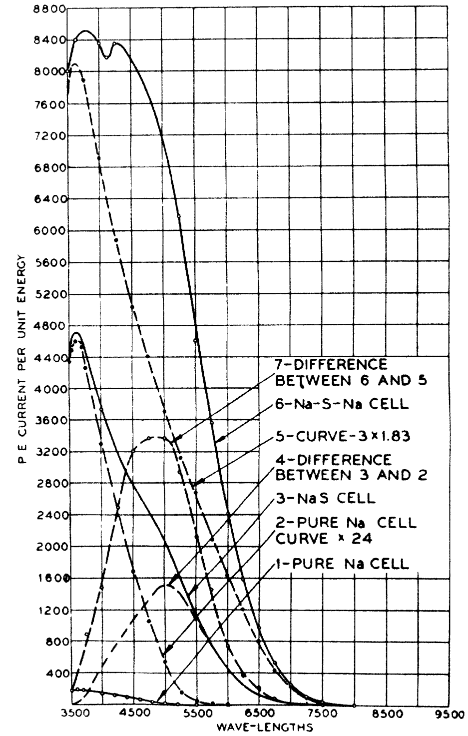


Fig. 11.

Fig. 10. Spectral response curve for sodium-sulphur vapor cell after deposition of a film of the mixture on the surface.

Fig. 11. Curves analyzing the increased sensitivity of sodium-sulphur vapor cells throughout the spectrum.

At this stage in the development of these cells, air at atmospheric pressure was admitted onto the surface. Upon re-evacuation the cell showed absolutely no response to light of any color. By applying a point flame near the edge of the cell window momentarily and producing a vapor of sodium plus the adsorbed gases, a film deposited on the cathode surface which was strikingly sensitive to light. This experiment has been repeated with many cells and the same effect always occurs. It appears that the effect is a broadening of the new selective maximum on the long wave side with a shift of the long wave limit to approximately 1μ, as shown in Fig. 12. Fig. 13 shows that pure Na surfaces can be sensitized to light of long wave-lengths by air and oxygen alone, but comparison with Figs. 12 and 14 indicates the advantage of the presence of sulphur vapor.

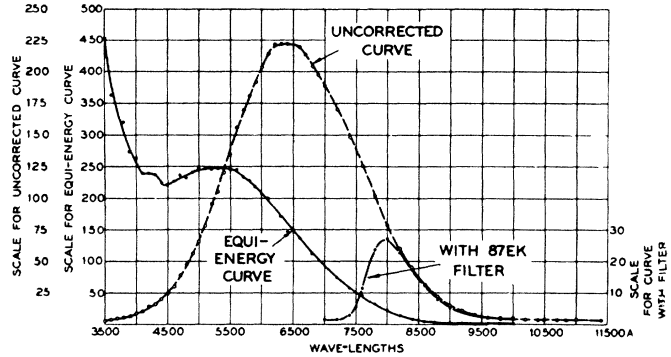


Fig. 12. Curves showing spectral distribution of sensitivity and long wave limits for sodium-sulphur-air cell. Actual electrometer readings are plotted in the broken curve, and current per unit energy in the so-called equi-energy curves.

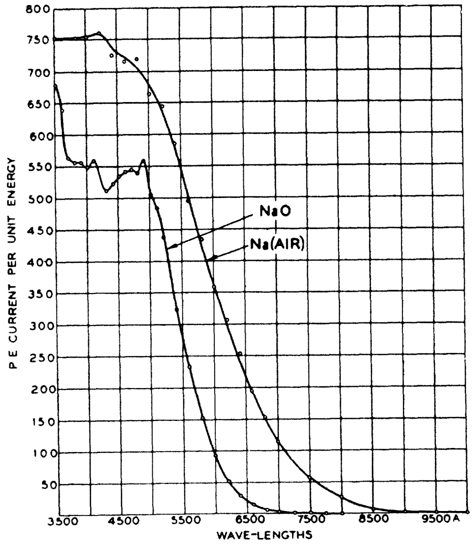


Fig. 13. Spectral response curves for sodium photoelectric cells treated with oxygen and air alone.

In Fig. 15 are given voltage-current curves for a typical potassium cell treated with sulphur vapor, a sodium cell similarly treated, another such

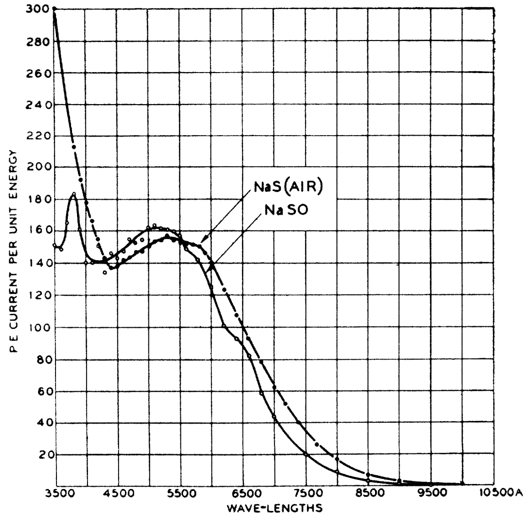
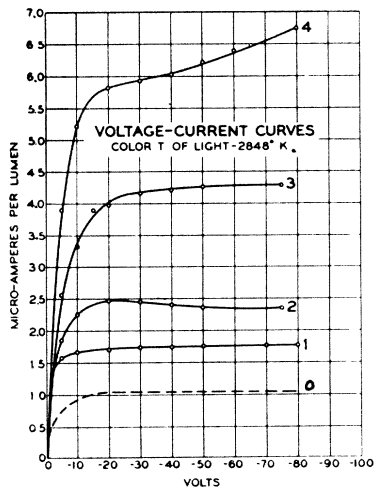


Fig. 14. Spectral distribution of sensitivity for sodium cells treated with sulphur and oxygen, and sulphur and air.



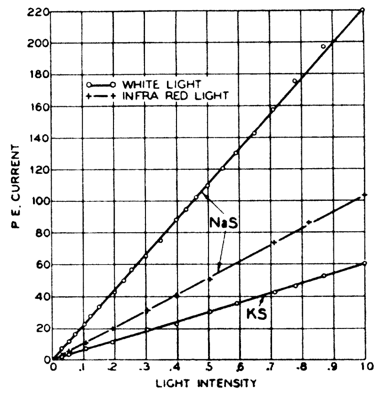


Fig. 15. Fig. 16.

Fig. 15. Voltage-current curves for five different types of vacuum photoelectric cells when irradiated with light of color temperature 2848°K. 0—Potassium hydride cell. 1—Potassium-sulphur vapor cell. 2—Sodium-sulphur vapor cell. 3—Sodium-sulphur vapor cell with film on cathode. 4—Sodium-sulphur-air cell.

Fig. 16. Showing proportionality of response of sodium and potassium-sulphur vapor cells to white light and to infrared light.

sodium cell with a thin film deposited on top of the dielectric, and finally a sodium cell treated with both sulphur vapor and air as described above. None of these cells were gas filled so the ordinates represent true emissions from the surface. These emissions are in terms of microamperes per lumen, and the color temperature of the exciting light was 2848°K.

C. PROPORTIONALITY OF RESPONSE TO LIGHT

The relationship between the light intensity and photoelectric current was checked over an extensive range for both potassium and sodium surfaces sensitized by the methods described above. The results are depicted by the straight lines in Fig. 16. The variations in light intensity were effected by moving the lamp source along a photometer track. The measurements were made on a Compton electrometer, using the steady deflection method. The same linearity of response was noted when using a No. 87 EK filter (visually opaque) in the path of the light. This filter transmitted only light of greater wave-length than that to which the pure metals respond.

D. ATTEMPTS TO IDENTIFY THE ACTIVATING GAS IN THE VAPORS FROM SULPHUR

The words "sulphur vapor" have been used advisedly in the foregoing presentation, for it was early discovered that the actual sublimation of sulphur onto the surface was not essential. In fact, equally good cells were made with only the volatile gases liberated from sulphur on heating. These gases could be held in a liquid air trap between the sulphur and the cell, and then by lowering the liquid air flask properly, the amount of gas actually entering the coated cell could be accurately controlled.

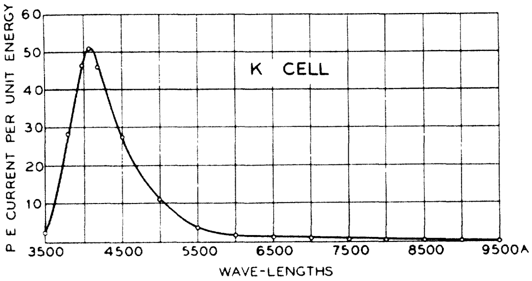


Fig. 17. Spectral response of a potassium photoelectric cell into which an unnoticeably small amount of vapor from sulphur had passed.

A surprising observation was that vapor in such small quantities as to be scarcely detectable with an ionization manometer gauge began to increase the sensitivity as soon as it entered the cell. In a way this was a fortunate discovery, for the amount of gas actually occluded or contained in commercial flowers of sulphur was decidedly small. Yet when a potassium cell with a side arm containing sulphur was sealed off the pump station, and a curve taken showing the spectral distribution of response to light (Fig. 17), there was appreciable sensitivity out to 1μ. Evidently some gas had been liberated from the sulphur, but the amount was too small to be detected. This emphasizes the importance of taking added precautions against the presence of gas on surfaces to be used in determining the long wave limits of pure alkali metals, and suggests the likely cause for the wide discrepancies sometimes found in literature.

The question as to the nature of the activating gas contained in sulphur was a challenging one since that gas was present in such small quantities.

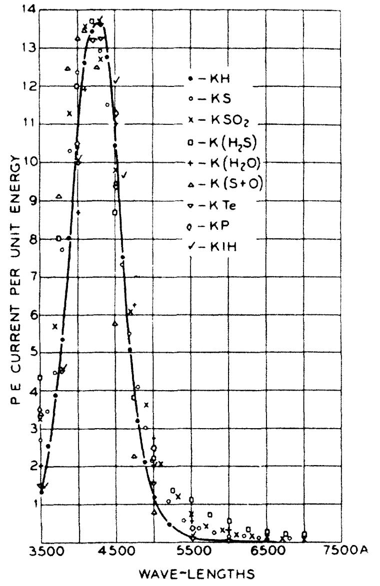


Fig. 18.

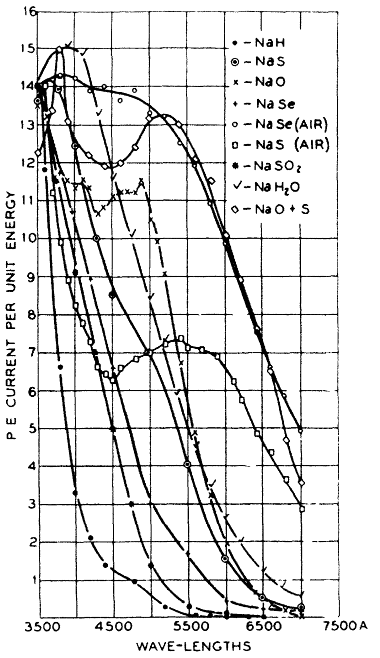


Fig. 19.

Fig. 18. Spectral response of potassium photoelectric cells, the cathodes of which were treated respectively with hydrogen, sulphur vapor, sulphur dioxide, hydrogen sulphide, water vapor, oxygen and sulphur vapor, tellurium vapor, phosphorous vapor and iodine vapor. The ordinates at the maximum are made equal.

Fig. 19. Spectral distribution of sensitivity of sodium photoelectric cells treated with hydrogen, sulphur vapor, oxygen, selenium vapor, sulphur-dioxide, water vapor, oxygen and sulphur, and selenium and sulphur with air. These curves are corrected to correspond at approximately 3500A.

It certainly was not air, hydrogen, nitrogen or oxygen, for these gases could not be condensed at liquid air temperatures. It therefore seemed plausible to suppose that it was water vapor, hydrogen-sulphide or sulphur-dioxide; and direct tests were made to find how these gases act.

A large number of potassium and sodium cells were made, the coating of each being treated with one of the mentioned gases. All of the spectral response curves for potassium cells had selective maxima in the blue at approximately the same wave-length, and the long wave limit did not vary appreciably from one cell to another. The gas producing results on potassium most nearly like those observed when using sulphur vapor was SO_2, the only one to give the bright golden color and the one producing the most sensitive surfaces to unresolved light.

In Fig. 18 curves depicting the spectral distribution of electron emission are given for potassium cells sensitized with sulphur vapor, sulphur dioxide, hydrogen sulphide, water vapor, sulphur vapor plus oxygen, tellurium vapor, phosphorous vapor and iodine vapor. In all these cases it will be noticed that the selective maximum appeared at approximately the same wave-length, but generally was shifted to somewhat smaller values when sulphur was present in the activating gas. We thus find nothing to support Wiedmann's idea[8] that the position of the maximum varies with the nature of the gas. It may be, however, that the relative *magnitudes* of the newly appearing maxima are influenced by the composition of the surface films.

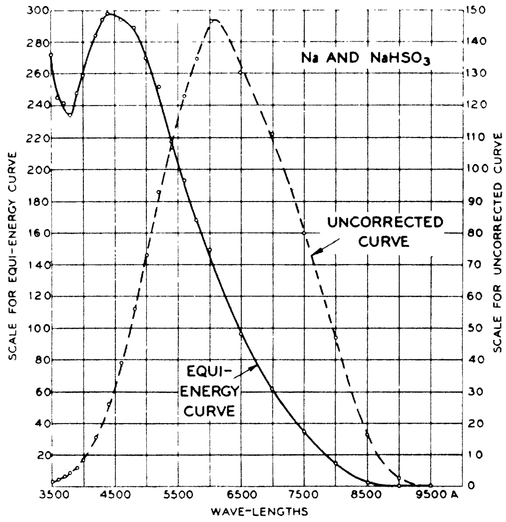


Fig. 20. Spectral response of sodium cell treated with sodium-bisulphite vapor.

With sodium the different gases produced markedly different curves (Fig. 19) and this gives us a better chance of identifying the vapor proceeding from the sulphur. In this case, it turned out that water vapor yielded the curve most resembling that due to the sulphur vapors, and incidentally colored the surface with a similar tint (dull grey); while sulphur dioxide alone provided a very different curve.

There seemed only one conclusion to draw from these tests. The activating vapor liberated from commercial flowers of sulphur must have been

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[8] G. Wiedmann, Verh, d. D. Phys. Ges. **16,** 343 (1915).

a combination of water vapor and sulphur dioxide,[9] and the dielectric films formed must have been sodium and potassium bisulphites. This conclusion seemed the more plausible when it was recalled that the sulphonic radical $SO_2 \cdot OH$ is an important radical in many organic dyes, and that investigators in the Eastman Research laboratory have succeeded in sensitizing photographic plates to light well into the infrared by the use of sodium bisulphite $NaHSO_3$.[10] A sodium cell was therefore made substituting sodium bisulphite for sulphur, and the spectral response of this cell (Fig. 20) was very similar to that obtained with sulphur and air. Moreover, the response was in almost identically the same spectral region to which the photographic plate treated with $NaHSO_3$ responded. The close correlation between these results in the fields of photoelectricity and photography suggests a common cause of the red sensitivity.

E. Sensitization of Sodium and Potassium Surfaces by Organic Dyes

There was no reason to suppose that sodium bisulphite is the only substance used in photography which could be applied in photoelectricity. Accordingly, other sensitizing dyes were introduced onto the light sensitive surfaces of alkali metals, and marked increases in photoelectric emission noted. In every case the amount of dye required was very small, as in plate sensitizing. The colors appearing on the cathode surfaces especially when thin films of sodium and potassium were added on top of the already treated surfaces were varied and beautiful.

Some of the side tubes containing the dyes had to be immersed in liquid air to prevent vaporization with possible decomposition under action of the pump. Others had to be warmed before they sublimed, and in such cases it is not only possible but likely that partial chemical decomposition occurred. In fact, Herndon and Reid's[11] study of the decomposition products of various alcohols, organic acids, acetates, benzenes, phenols, etc. upon heating to 400° suggests that the more complicated compounds break up into simple ones at considerably lower temperatures. Nevertheless, the well-known organic radicals which produce the absorption bands in the visible region, as the methyl group CH_3, the nitroxyl group NO_2, the amido group NH_2, the bromine group, the methoxyl group CH_3O, the carboxyl group $CO \cdot OH$ and the sulphonic group SO_2OH, and many others probably are fairly stable.

The first dyes used contained the sulphonic radical and are not commonly used in photography. They were kept in a side tube beyond a liquid air trap, and heated after the alkali metal coating was made. When they were first heated, some gas passed through the liquid air trap into the cell and was

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[9] More recently Dr. G. T. Kohman of the Bell Telephone Laboratories has made a very ingenious analysis of the gases evolved from flowers of sulphur on heating and found water vapor and sulphur dioxide to be contained in greatest amounts, with also considerable hydrogen sulphide.

[10] Capstaff and Bullock, Brit. J. Phot. **67,** 719 (1920).

[11] L. R. Herndon and E. E. Reid, J.A.C.S. **50,** 3066 (1928).

pumped out. This was probably nitrogen, hydrogen, or dry oxygen, or possibly some hydrocarbon compound, for it did not react with the alkali metal. The gas retained in the liquid air trap was very effective in sensitizing the metallic surface of the cell when allowed to enter in small quantities. A very thin film of the alkali metal deposited on the colored surface always enhanced the emission. In Fig. 21(a) are curves showing the response, in the visible and infrared, of sodium cells treated with the isomeric compounds tropaeolin 000 No. 1 $[HO \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4 \cdot SO_3Na]$ and sodium indigo disulphonate. Both compared favorably with the sodium-sulphur air cells

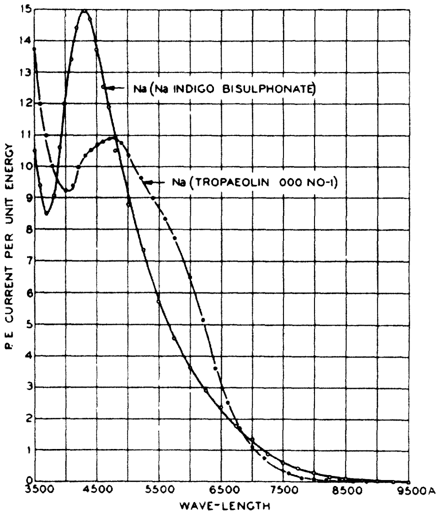

Fig. 21. (a) Spectral response curves for sodium photoelectric cells treated with the vapors of tropaeolin 000 No. 1 and sodium indigo disulphonate.

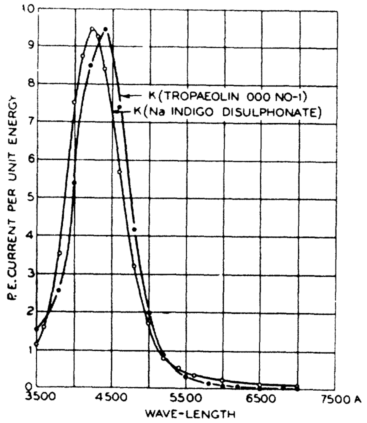

Fig. 21. (b) Spectral response curves for potassium photoelectric cells treated with the vapors of tropaeolin 000 No. 1 and sodium indigo disulphonate.

described in a previous section. Curves for the corresponding potassium coated cells, using these dyes, are given in Fig. 21(b).

To determine whether or not the sensitizing action was limited to compounds containing sulphur, a cell was made with rosaniline base [$OH \cdot C(C_6H_4NH_2)_3$] and a sodium coating. Although no sulphur was contained in this compound, the surface treated showed a good response to light throughout the visible and near infrared, as shown in Fig. 22.

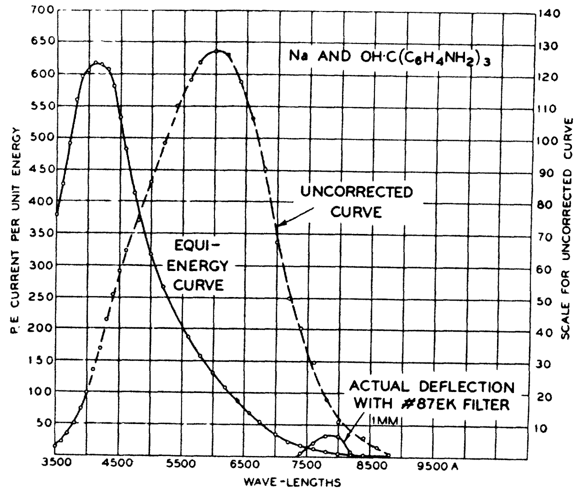

Fig. 22. Spectral response curve for a sodium cell treated with rosaniline base.

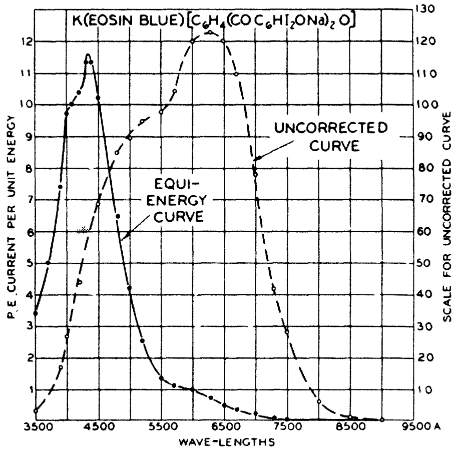

Fig. 23. Spectral response curve for a potassium photoelectric cell treated with eosin blue.

The remainder of the experiments to be reported in this section involve sensitizing dyes used in photography. Because of its historical importance, (it was first used to sensitize photographic plates to green and yellow light in 1882) eosin $[C_6H_4(COC_6HI_2\,ONa)_2O]$ was tried first. Although it brought about a decided increase in sensitivity, it was not so satisfactory as many others. In Fig. 23 is reproduced a spectral distribution curve for a potassium-eosin cell, showing the presence of the new maximum at longer wave-lengths very strikingly. The peculiar shape of the regular selective maximum will be cited again in the discussion to follow. There appears to be a new peak at a slightly shorter wave-length.

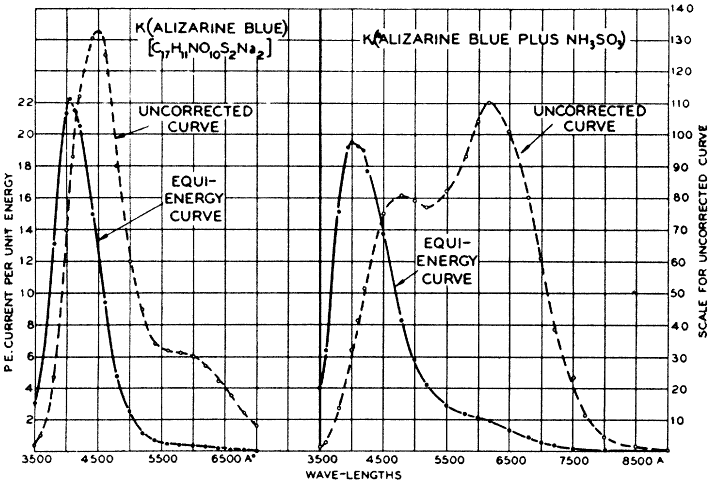

Fig. 24. (a) Spectral response curves for a potassium photoelectric cell treated with alizarine blue alone and one treated with alizarine blue plus ammonium sulphite.

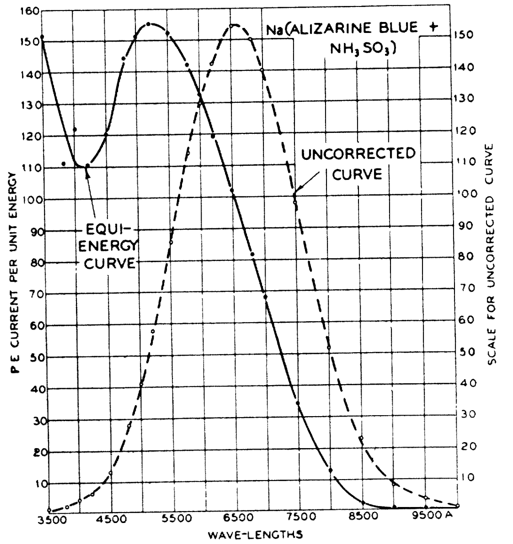

Fig. 24. (b) Spectral response curve for a sodium photoelectric cell treated with alizarine blue and ammonium sulphite.

Some have claimed astonishing results in sensitizing photographic plates to red by using alizarine blue [$C_{17}H_{11}NO_{10}S_2Na_2$];[12] and plates treated in addition with ammonia, have been reported sensitive out to about 1μ. In Fig. 24(a) is found a typical photoelectric emission curve for a potassium coating treated with alizarine blue and another curve for potassium treated also with the vapor from ammonium sulphite (NH_3SO_3). In Fig. 24(b) is a curve for sodium similarly treated. These curves show a response to light of all wave-lengths under 1 μ, with the new maxima appearing at the same position as for the sulphur vapor cells. Here again is a close correlation between results obtained in the sensitizing of photoelectric cells and photographic plates.

Similar results attended the use of dicyanine, especially with addition of ammonium sulphite, and other dyes carrying the latter part of the same word in their trade names, as kryptocyanine and neocyanine. The spectral regions wherein these dyes are effective sensitizers of photographic plates is published in communication No. 255[13] of the Eastman Research Laboratories where the latter two dyes were developed. Kryptocyanine should be better in the near infrared than dicyanine which in turn should be better than cyanine ($C_{29}H_{35}N_2I$). All of these indications were borne out on photoelectric cells, the dicyanine causing a greater electron emission from alkali metal surfaces than cyanine, and very small amounts of kryptocyanine producing one of the broadest selective bands so far observed in the spectral distribution curve for sodium cells. This last mentioned curve is found in Fig. 25.

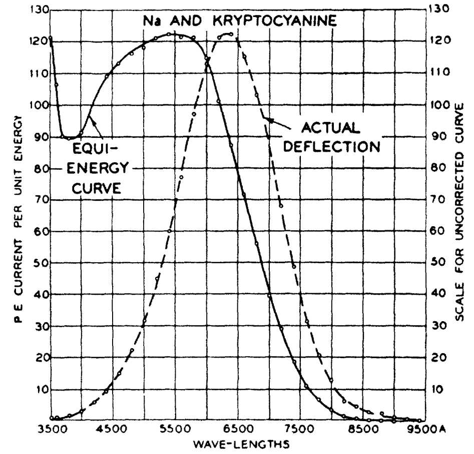

Fig. 25. Curve showing strikingly broad selective maximum in the spectral response curve for a sodium photoelectric cell treated with kryptocyanine.

F. Sensitization by Colorless Dielectrics

The position of the new maximum seems to be characteristic of the light sensitive metal and not the dielectric on its surface. It appeared likely,

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[12] Scoble, Phot. J. **46**, 190 (1906).

[13] M. L. Dundon, A. L. Schoerr, R. M. Briggs, J.O.S.A. and R.S.I. **12**, 397 (1926).

therefore, that any dielectric regardless of the peculiarities of its absorption spectrum, might bring out such a maximum. To test this, various colorless dielectrics and dielectrics practically transparent to visible light were substituted for the dyes. Most of these were liquids, but their vapors could easily be held in side tubes by means of liquid air. The technique employed in applying them was identical to that for the dyes.

Acetone ($CH_3\cdot CO\cdot CH_3$), *acetic acid* ($C_2H_4O_2$) *carbon bisulphide* (CS_2), *methyl alcohol* (CH_3OH), *carbon tetrachloride* (CCl_4), *benzene* (C_6H_6), *chloroform* ($CHCl_3$), *phenyl mustard oil* ($C_6H_5\text{-N-C}=S$), *nitrobenzene* ($C_6H_5NO_2$), and *water-vapor* (H_2O) were used with more or less success. And surprising though it may seem, benzene and water vapor were the most effective, the red sensitivity of sodium surfaces properly treated with them being especially marked, as shown in Fig. 26. There was absolutely no evidence of chemical action when benzene was admitted to the cell, even though a thin film of sodium was deposited on top of it. In fact, the surface of the completed photoelectric cell looked exactly like that of pure metallic sodium. This, of course, is not surprising since the alkali metals are preserved in benzene, but is cited here as evidence of the chemical purity of the sample used. In quite striking contrast to the behavior of benzene on sodium was that of water vapor, whose powerful affinity for the alkali metals makes it necessary to preserve them in benzene, oil, or sealed air-tight containers. Yet benzene and water vapor were alike in being able to increase photoelectron emissions from sodium and potassium surfaces.

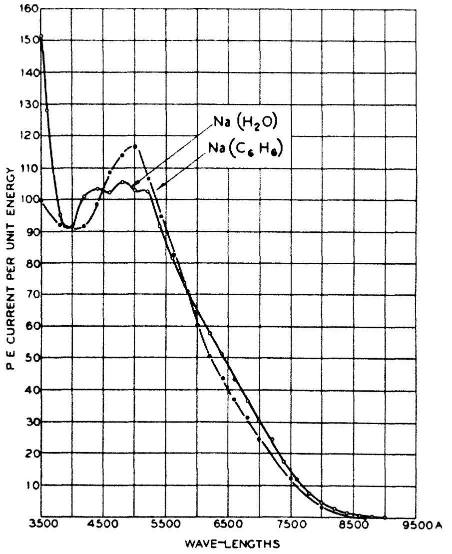

Fig. 26. Spectral response curves for sodium photoelectric cells treated with water vapor and with benzene.

In every case mentioned in the preceding paragraph, except that of CCl_4, an appreciable amount of sensitivity to red was developed. Moreover, the

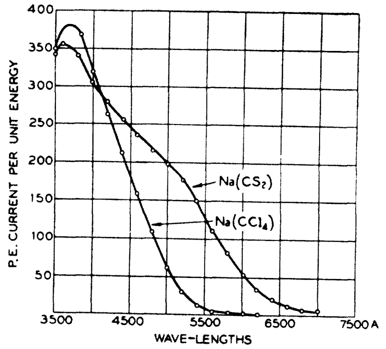

Fig. 27. Spectral response curves for sodium photoelectric cells treated with carbon bisulphide and with carbon tetrachloride.

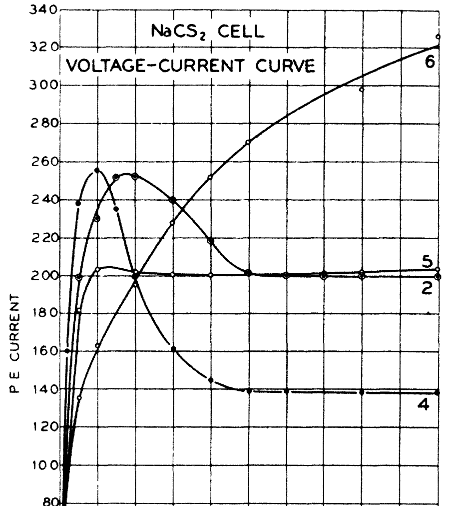

Fig. 28. Peculiarities noted in voltage-current curves for a sodium-carbon bisulphide photoelectric cell. 1—Supposedly pure sodium. 2—After first introduction of CS_2 on sodium surface. 2R—Same as 2 but for irradiation with red light only. 3—After additional CS_2 was introduced onto the surface. 4—After a film of sodium had been deposited from near the cell window. 4R—Same as 4 but for illumination with red light only. 5—Light focussed on cathode opposite cell window. 6—Light focussed on cathode adjacent cell window.

spectral distribution curves show evidence of a new maximum in the photoelectric emission curve near λ4800A for sodium and a much less pronounced peak at approximately λ6200A for potassium. When carbon tetrachloride was used no deflection of the galvanometer was observed when the exciting light was passed through a red filter, cutting out all wave-lengths under 6000A. In Fig. 27 are plotted wave-length vs. current curves for sodium surfaces sensitized with carbon tetrachloride and carbon bisulphide.

When working with carbon bisulphide (CS_2) and nitrobenzene ($C_6H_5NO_2$) the previously described peak in the voltage-current curve at low voltages was strikingly prominent. At one time during the treatment of sodium with CS_2 the current output with the cathode 15 volts negative was four to five times its value when this voltage was increased to 100 volts. A record of the change in shape of these curves as the sensitization process was carried out is included in Fig. 28. These will be discussed with those in Fig. 2 and 3 in the next section.

G. Discussion of Results

A great mass of data has been presented. It now remains to be seen whether or not they can be correlated and interpreted. In all, over two hundred photoelectric cells involving the principles and technique herein discussed have been made, and most of them carefully studied. The collection of curves presented in the preceding sections of this paper may or may not in every case refer to the best cell which could possibly be made with the stated materials; but they do display the properties of the cell when made according to the best technique at that time known.

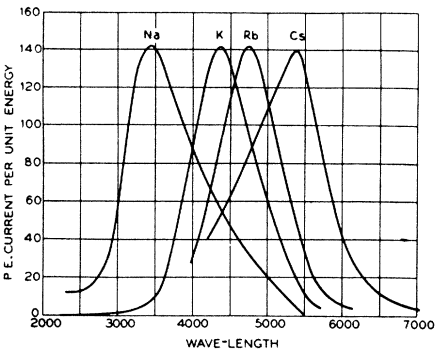

Fig. 29. Spectral response curves for the alkali metals. Curves for sodium and potassium reproduced from Pohl and Pringsheim[7] and those for rubidium and caesium from Miss Seiler.[5]

A survey of the data presented in the form of spectral response curves revealed that the properties of the cells depended very much on the metal, very little on the dielectric. As pointed out previously (Fig. 11) each curve could be represented as the sum of the "regular" curve for the pure metal and a second curve with a maximum at longer waves. Only the *relative magnitudes* of the ordinates of these two curves seemed to be a function of the dielectric. The so-called "regular" curves for the pure alkali metals are shown in Fig. 29. Each one will be seen to resemble a resonance curve, the area underneath being more or less symmetrically located on either side of the wave-length of light producing the greatest photoelectric current. These curves are not alone characteristic of the multiply distilled metals, but are also characteristic of these metals after a glow discharge has been passed through hydrogen at a pressure of a few millimeters on the surface. This fact caused Pohl and Pringsheim[14] to refer to the metallic hydride surfaces as colloidal metal surfaces and attribute the increased response of such surfaces to light to the greater ease with which electrons might escape from tiny globules. This same fact caused Hallwachs and Wiedmann[15] to claim that the photoelectric effect was a gas-metal phenomenon and that the maxima in the curves shown in Fig. 29 were dependent on the presence of hydrogen. At this stage in our discussion it is the *existence* of these maxima in the "regular" curves rather than the *cause* to which attention is called.

The "second" curve referred to above appeared as the "regular" curve shifted to longer wave-lengths. The amount of this shift was approximately the same for all cases excepting the ones in which sulphur or selenium plus oxygen or air and certain organic dyes, as kryptocyanine, were among the activating agents, in which cases it was somewhat greater, and the new maximum broader, as illustrated in Fig. 19. Slight variations in the separations of the two maxima, when several dielectrics were used, were dependent on the relative amounts of the different materials.

1. *Role of water vapor.* This analysis of the spectral response curves suggested that there is a single activating agent common to all the dielectrics introduced onto the alkali metal surfaces, with the possibility of one or more others in a few cases. Certainly it must be conceded that water vapor may have been present in every case. Every effort was made to eliminate it, the glass bulbs being carefully and thoroughly heated during the evacuating process. But, as mentioned earlier, the substances which were evaporated or sublimed onto the cathodes may have contained water. The glass tubes containing them could not be heated sufficiently to drive out all moisture before the alkali metal coatings were made. With liquids, it was necessary to immerse the side arm containing them in liquid air to keep them from evaporating and being pumped out. Moreover, the bulky, complex organic dye compounds usually occur in the form of very fine crystalline granules, undoubtedly containing water in small quantities. Some of the substances may have decomposed with formation of water vapor. There was no assurance that the samples of liquid dielectrics were absolutely water free, even though they were obtained from a reliable chemical house as certified chemically pure material. Take, for instance, benzene, a liquid easily obtained as "chemically pure" yet Manley[16] reports experiments which seem to

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[14] R. Pohl and P. Pringsheim, Verh. d. D. Phys. Ges. **13,** 219 (1911); Verh. d. D. Phys. Ges. **15,** 173 (1913).

[15] G. Wiedmann and W. Hallwachs, Verh. d. D. Phys. Ges. **16,** 107 (1914); G. Wiedmann, reference 8.

[16] J. J. Manley, Nature **123,** 907 (1929).

indicate that benzene, when exposed to air, takes up moisture and holds it tenaciously. Certainly, the difficulties involved in handling liquids in an evacuated system make it impossible to eliminate water vapor altogether from the system.

Although the amount of water that could have been present with the dielectric was admittedly always small, it may not have been negligible. As a matter of fact, many of the experiments seemed to indicate that even *minute traces of moisture* were sufficient to sensitize alkali metal surfaces. One experiment consisted in sealing an empty glass tube on the side of a bulb and then during the pumping process immersing the tube in liquid air. After the bulb was coated, mere removal of the liquid air from the side tube permitted sufficient moisture to fall onto the metal coating to increase its response greatly. The characteristic of such a sensitized surface could be represented by the spectral response curve of Fig. 26. However, the total emission was not nearly so great as in the case of the cells containing sulphur vapor or organic dyes. It appeared, therefore, that the presence of water vapor in small quantities may have been advantageous, but was certainly not alone responsible for the whole of the observed increase in the photoelectric effect.

Perhaps the water vapor present with some such dielectric as sulphur was taken up as water of crystallization as alkali metal sulphides or sulphates were formed on the cathode surface. It is rather significant in this respect that the oxides, sulphides and sulphates of sodium and potassium quite generally hydrate if water is present, and the appearance of these hydrated crystalline forms resemble those of the photoelectric cell cathodes prepared as described earlier in this paper.[17] This indicates that the surface films may have a definite configuration and the molecules a regular alignment, which really would be expected, for polar compounds in general are favorable to association, and this, as Gerlach[18] commented, is a "preliminary stage of microcrystalline character." It is a well-known observation that while water of crystallization plays a definite role in the crystal structure, it reacts toward radiant energy as water vapor in its free liquid state.[19]

In connection with these remarks on water of crystalization, attention is called to the studies of Predwoditilew and Blinow[20] concerning the photoelectric emission of finely powdered crystalline sulphates. They announced a simple relation between the photoelectric current and the water of crystallization.

It occurred to us that the dielectric substance may form a surface film which reduces the work function; the molecules may well have been so aligned as to act as tiny grids setting up powerful fields which aided in pulling electrons from the alkali metals surface. This idea has been effectively

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[17] H. Bottger, Liebig's Ann. **223**, 335 (1884).

[18] W. Gerlach, "Matter, Electricity, Energy," p. 65–66.

[19] W. W. Coblentz, Publication No. 35, p. 56 Carnegie Inst. of Washington, Bull. Bur. Stand. **7**, 4, 619 (1911).

[20] A. Predwoditelew and W. Blinow, Zeits. f. Physik **42**, 60 (1927).

used in interpreting long wave shifts, such as are caused by oxide coatings on filaments of thermionic tubes;[21] but we do not see how it could explain the new selective maximum appearing simultaneously with the shift.

Richardson and Young[22] had a theory that the two peaks in their spectral response curves for potassium treated with water vapor and flashed in hydrogen were due to the presence of multiple thresholds on a spotted cathode; but there is nothing in their discussion to explain why the selective maxima occur at the same wave-length for all dielectrics on a given metal; unless, of course, water vapor be the activating agent in them and act independently of and more effectively than any other substances with which it might be mixed.

2. *Lack of correlation between selective maxima and absorption bands in the visible.* We found no relation between the absorbing power of the various dielectrics for *visible* light and the sensitization which they brought about, although this conclusion might be modified if the actual absorption of the deposited films of these substances could be observed. As an example of this might be mentioned the case of water vapor with its weak absorption in the visible, producing better results than cyanine at the particular wave-lengths where this dye has powerful selective absorption (4500–6500A).[23]

H. Theoretical Considerations

1. *Correlation of separation of maxima with infrared vibration-rotation spectra of the dielectrics.* The absorption of light by water vapor increases in the direction of increasing wave-length, and is very strong in the near infrared. It consists of a series of lines or narrow bands so related that if the frequencies of the powerful absorption bands near 6μ and 3μ be taken as fundamentals, other bands can be regarded as the first, second, and third harmonics of

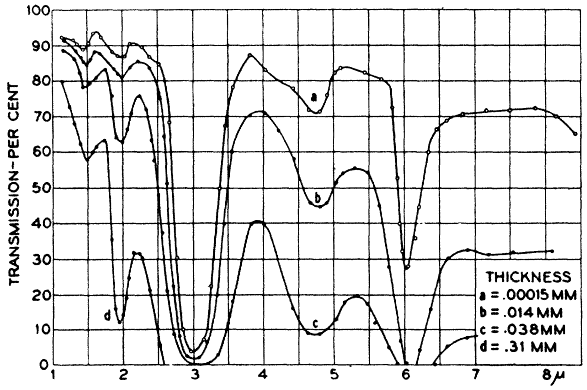

Fig. 30. Absorption spectra of thin films of water. Reproduced from Bull. Bur. Stand. **7**, 4, 631.[19]

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[21] J. A. Becker, Phys. Rev. **28**, 341 (1926).

[22] O. W. Richardson and A. F. A. Young, Roy. Soc. Proc. **A107**; 377 (1925).

[23] Bull. Bur. Standards No. 422 (1922).

these.[24] Also these frequencies seem to combine or add up to give other spectral lines. In general, frequencies corresponding to wave-lengths less than 1.5μ are not so strong (Fig. 30), but in the form of vapor or water of crystallization[25] the higher harmonics become sharper and more pronounced (Fig. 31), a line at 1.119μ being almost as strong as the 1.47μ line into which the 1.5μ band resolves itself. This absorption series, the "vibration-rotation spectrum," is due to interatomic vibrations within the molecule, or more specifically to vibrations set up between the hydrogen and oxygen atomic nuclei.

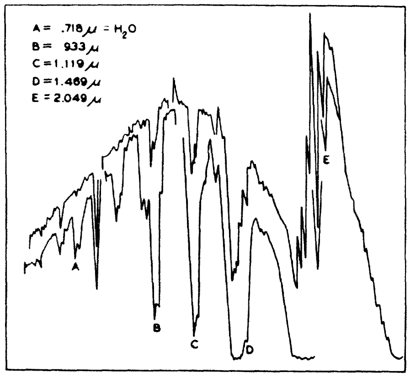

Fig. 31. Bolographic energy curves of the solar spectrum of a 60° glass prism, the upper one taken in February when the humidity was low and the lower one in September when the humidity was high. Curves reproduced after Coblentz from Fowle: Smithsonian Misc. Coll. Vol. **47,** No. 1468, (1904).

Now there seems to be considerable evidence that the increased photoelectric response is in some way, directly or indirectly, connected with this or a similar spectrum. For, in the first place, such absorption bands are quite characteristic of all compounds containing an oxygen-hydrogen carbon-hydrogen or nitrogen-hydrogen linkage, as shown in Table III.

TABLE III.

O-H Linkage[26]	C-H Linkage[27]	N-H Linkage[27]
3.06μ	3.28μ	2.90μ
1.469	1.68	1.50
1.119	1.145	1.03
.933	.874	.790
.718	.713	.648

There are other important bands of longer wave-length than 3μ, the ones near 6μ being particularly strong. However, (as pointed out by Ellis in discussing the bands listed here for the N-H linkage), the ones just tabulated

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[24] H. A. Rowland, Astrophys. J. **6,** (1897).

[25,26] W. W. Coblentz, reference 19.

[27] J. W. Ellis, Phys. Rev. **33,** 27 (1929), Frank. Inst. J. **208,** 4, 507 (1929).

are of particular interest, for the positions of the bands are seemingly independent of the presence or nature of the solvent.

Since a band-system of the foregoing type is found in the spectra of so many different compounds involving hydrogen, it is reasonable to suppose that the vibrations to which such bands are due, occur in the molecules formed by the vapors which we brought into contact with alkali-metal surfaces.

Now we have observed a very interesting pair of numerical agreements, which are probably more than mere coincidences. On evaluating the shift in frequency δ of the long wave limit and the selective maximum, which occurs when an alkali metal is affected by one of the vapors in question, we found:

(a) In many cases this frequency-shift is equal to the frequency corresponding to the wave-length 1.5μ, which is that of a strong band in many molecules of the stated kind;

(b) In certain other cases, notably where sodium surfaces were involved, the frequency-shift is equal to the frequency corresponding to some wavelength near 1μ, where there are other bands.

A couple of other things suggest that the presence of hydrogen may be essential to these shifts: viz. Wiedmann's[28] data which suggested to him that not only the shifts but the actual maxima themselves are due to hydrogen; and the fact that CCl_4 contains no hydrogen, has no absorption-bands in the near infrared (Abney and Festing[29]) and did not produce a frequency-shift, whereas $CHCl_3$, with its hydrogen-content and its vibration-bands, did produce one.

We make, then, the tentative hypothesis that the frequency-shifts are due to the presence of molecules having natural vibration-frequencies equal to these shifts; and attempt to explain why such molecules should have that particular effect.

It may be that when an alkali-metal atom is incorporated into a molecule having an O-H bond (for example) the resulting complex molecule possesses a natural frequency equal to that of the alkali-metal, diminished by that appropriate to the O-H bond. It is well known that two electrical or two mechanical systems with natural frequencies of their own may be coupled into compound systems having a frequency which is the difference of theirs (cf. for instance Hartley and Peterson)[30]. Something of the sort may occur here.

The newly-discovered phenomenon of the "Raman shift," however, offerred a very tempting explanation.

2. *The Raman shift as an explanation of the frequency-shift of the spectral response curves.* In the language of the quantum-theory of light, a "Raman shift"[31] occurs when a quantum or photon collides with a molecule, causes

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[28] G. Wiedmann, reference 8.

[29] W. de W. Abney and E. R. Festing, Phil. Trans. **172,** III, 887 (1881).

[30] R. V. L. Hartley, Abs. 48, Bull. Am. Phys. Soc. **3,** 7 (1928); E. Peterson, Bell. Lab. Record **7,** 6, 231 (1928).

[31] C. V. Raman, Ind. Journ. of Phys. **2,** 387 (1928); C. V. Raman and K. S. Krishnan, Roy. Soc. Lond. Proc. **A122,** A-789, 23 (1929).

the molecule to pass from its initial to another of its stationary states, receives the energy which the molecule gives up (or alternatively, gives up the energy which the molecules absorb) in making this transition, and flies off with energy correspondingly increased (or diminished). In the language of the wave-theory (Hartley[32]) a Raman shift occurs when the frequency p of an incident wave-train of light is modulated by the frequency q of a natural vibration of the molecule on which the light falls, the shifted wave-trains being the "sidebands" of frequencies $p+q$, $p-q$, $2p-q$, etc.

Now suppose that some of the quanta striking the treated alkali-metal surface collide with molecules which are not in the normal, but in some excited state of vibration; and that in such a case, the molecule transfers to the quantum the amount of energy which it would release in the form of radiation, if it were spontaneously to relapse to a lower vibration-state; for instance, that it transfers the energy of one quantum of radiation of wave-length 1.5μ. Then the quanta which have made such collisions have their frequencies correspondingly augmented. If now they fall on the alkali metal and produce the photoeffect, it is the photoeffect proper to light of augmented frequency which they produce. The spectral-response curve would then be shifted because the frequency of the light itself is shifted before it reaches the photo-sensitive surface.

This idea was temporarily adopted as a working hypothesis; but a number of objections arose which are hard to surmount. In the first place, the sense of the shift is such that we must suppose the quanta to collide with molecules already excited. Now in a substance in thermal equilibrium, the proportion of molecules in any given state of excitation may be computed by Boltzmann's equation:

$$n = n_0 e^{(-\epsilon/kT)} \tag{1}$$

in which T stands for the temperature of the substance, k for the Boltzmann constant, n_0 for the number of molecules in the normal state or state of least energy, and ϵ for the energy of the given excited state referred to that of the normal state as zero. It seems unlikely that the proportion of excited molecules should be great enough to account for such results as those shown in Fig. 14 (for example) or in Fig. 32, where the "shifted" is as large as the regular maximum,—a result obtained when very thin films of potassium were flashed in hydrogen on oxidized copper plates. And it seemed doubly unlikely that the excited molecules should be numerous enough to explain the presence of such pronounced maxima at long wave-lengths as those shown in Fig. 7, where in the cases of curves (a) and (b) they are several times the magnitude of the regular maximum for caesium at λ5500A.

One would expect encounters in which quanta give energy to normal molecules to be far more abundant than encounters in which quanta receive energy from excited molecules. In other words, if p stands for the frequency of the incident light and q for that of the vibrating molecule, the $p-q$ frequency should be more intense than the $p+q$ frequency and possibly present

[32] R. V. L. Hartley, reference 30.

when the latter was not. There should then, be a new maximum, much stronger than the one which we have observed, located towards higher frequencies from the maximum characteristic of the pure metal. We were not fully equipped to investigate this region and so obtained no definite information. However, the curves for caesium cells (Fig. 7) show evidence of a maximum at higher frequencies, and also the shift of the λ4360 peak of

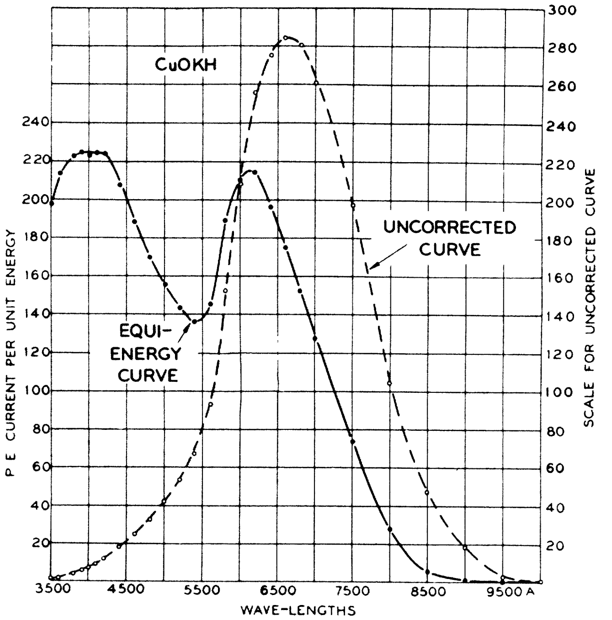

Fig. 32. Spectral response curve for a potassium film flashed in hydrogen on a copper-oxide plate

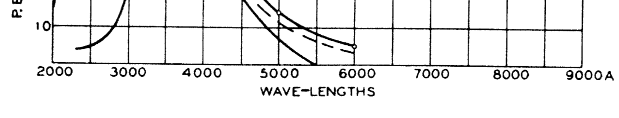

Fig. 33. Spectral response curves showing how Richardson's and Compton's observed double maxima for a sodium photoelectric cell appear as the regular selective maximum of Pohl and Pringsheim plus this maximum shifted to higher frequencies by an amount corresponding to the frequency of the λ0.718μ water vapor absorption line.

pure potassium to somewhat higher frequencies (Fig. 5) upon treatment with dielectrics might be explained by assuming the $p-q$ frequencies greater than the $p+q$ and taking q equal to the frequency of the intense 3μ water vapor band. Richardson and Compton have published a curve for sodium showing a peak at λ2270A in addition to the regular one at λ3600A. Since the cell they used had electrodes sealed in with cement which would prevent thorough baking, water vapor was probably present. The ultraviolet peak could be explained as a $p-q$ frequency if we put q for the frequency of the 0.718μ line of the vibration-rotation spectrum of water vapor. In Fig. 33 is plotted a curve based on the assumption that this $p-q$ frequency produces

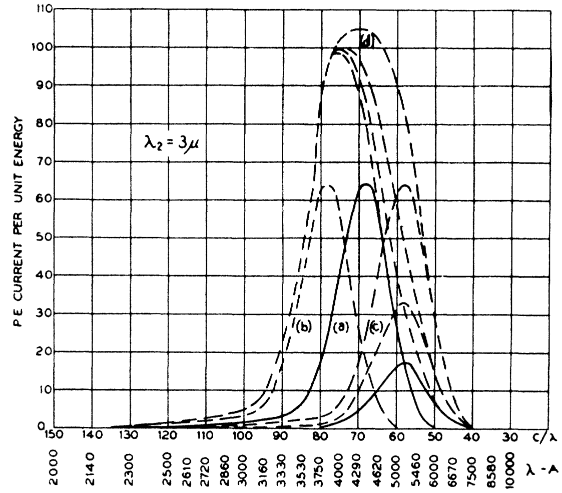

Fig. 34. Theoretical modifications of the spectral response curve for potassium photoelectric cells, assuming modulation of the incident light frequency p by the strong 3μ absorption band of water vapor. a) Curve for pure potassium (Pohl and Pringsheim). b) Curve (a) shifted to higher frequencies by an amount corresponding to $q = c/3\mu$ to show the effect of the $p-q$ side frequencies. c) Curve (a) shifted to lower frequencies by a similar amount to show the effect of the $p+q$ side frequencies. d) Composite curves assuming the presence of the incident light frequency p and the side frequencies $p \pm q$, illustrating the shift of the maximum to shorter wave-lengths with a decrease in the intensity of the $p+q$ sideband.

a maximum as strong as the unmodulated p frequency,—an assumption probably false. The shift of the long wave limit might also be taken to indicate the presence of a weak positive side frequency, also.

In Figs. 34 and 35 are plotted some theoretical curves for potassium cathodes, assuming the $p \pm q$ frequencies to be operative with varying intensities. In Fig. 36 is illustrated the close agreement between the theoretical and observed values. Similar curves for sodium may be shown.

We might avoid the need for postulating a transfer of energy to quanta from excited molecules by assuming that two quanta simultaneously strike a normal molecule and excite it, and a single quantum is then radiated having energy equal to the sum of their energies less that required to excite the molecule. This seems a highly improbable event; but in any case the experiments which we are now about to describe exclude it, for if the theory were correct the kinetic energy of the emerging electrons would be equal to $2h\nu$ minus the surface work function, instead of to $h\nu$ minus this function.

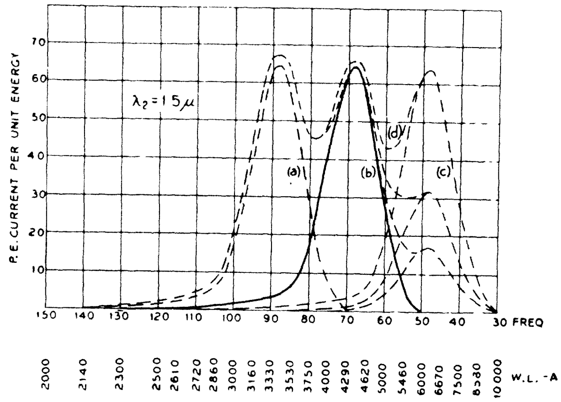

Fig. 35. Theoretical modifications of the spectral response curve for potassium photo electric cells, assuming modulation of the incident light frequency p by the 1.5μ absorption band of water vapor. a) Curve for pure potassium (Pohl and Pringsheim). b) Curve (a) shifted to higher frequencies by an amount corresponding to $q=c/1.5\mu$ to show the effect of the $p-q$ side frequencies. c) Curve (a) shifted to lower frequencies by a similar amount to show the effect of the $p+q$ side frequencies. d) Composite curves assuming the presence of the incident light frequency p, and the side frequencies $p\pm q$, showing how the magnitude of selective maximum at λ6200A might depend on the intensity of the $p+q$ sideband.

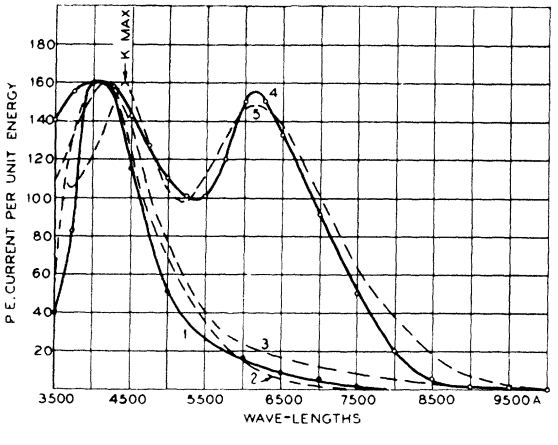

Fig. 36. 1—Experimental spectral response curve for a potassium cell after preliminary treatment with a dielectric. 2—Theoretical curve for a combination of light frequencies p and $p+q$, where $q=c/3\mu$ and the intensity of $p+q$ is considered one quarter that of the incident frequency p. 3—Theoretical curve for a combination of light frequencies p and $p+q$ where $q=c/1.5\mu$ and the intensity of $p+q$ is one-eighth that of p. 4—Experimental spectral response for a potassium film flashed in hydrogen on a copper-oxide plate. 5—Theoretical curve for a combination of light frequencies p and $p\pm q[q=c/1.5\mu]$ all of equal intensity.

However, the gravest objection to the "Raman Shift" theory is that it requires that the electrons should receive the energy $h(\nu+\delta)$ rather than the energy $h\nu$ when the substance is illuminated by light of frequency ν; so that the adverse voltage as read on the voltmeter which is required to stop the fastest electrons, the "apparent stopping potential," should be increased by the amount corresponding to $h\delta$ when the vapor is admitted to the metal. No such effect has ever been observed; but as the interpretation of the data requires an allowance for contact potential, this point must be left for discussion in the next section.

3. *Accurate determination of the stopping-potential vs. frequency curve and evaluation of h.* According to the well-known Einstein equation

$$Ve = \tfrac{1}{2}mv^2 = h(\nu - \nu_0) \qquad (2)$$

the graph of stopping potential versus frequency should be a straight line of slope h. Our experiments have verified this prediction over a range of frequencies heretofore unemployed and extending into the infrared, have led to a very precise value of h, and have incidentally eliminated the idea mentioned above that a frequency $(2p-q)$ might result from the interaction of light with the molecules; for that idea would require a slope equal to $2h$.

A photoelectric cell was specially designed to avoid the deposition of photosensitive materials on the anode, for this is fatal to accurate determinations of stopping potentials as will be explained directly. As will be seen from Fig. 37, the cathode could be coated with freshly distilled sodium in one end of the tube and then transferred in vacuum to the other end where it became a central cathode surrounded by a cylindrical anode made of soot-coated nickel. Again at any time the cathode could be removed to its original position for further sensitization.

The potential drop across the electrodes of such a cell read on the voltmeter is of course not the true one; allowance must be made for contact difference of potential. The voltage at which the current just saturates would be that for the true potential drop equal to zero, if the anode completely encompassed the cathode. When there are small openings in the anode, such as a hole through which to introduce the exciting light, a slight positive potential is required to produce saturation of the photoelectric current. It is always possible, however, to find the effective or true zero voltage if the long wave limit is carefully determined, as will soon be shown. The true stopping-potential is then measured by the distance, along the axis of voltage, from that point to the point where the current just reaches zero. This last would not be true if the cylinder emitted electrons, for then there would be a "reverse" current when the field was so directed as to drive electrons from it to the central electrode, and the net current would vanish when this just balanced the direct current, not when the direct current itself vanished. But in our experiments the cylinder was not photosensitive at all, and there were never any *reverse* currents.

The photoelectric currents were measured by means of a Compton quadrant electrometer, using the constant deflection method. The cathode was illuminated sometimes by the highly resolved light of a glowing tungsten filament, sometimes by means of the monochromatic lines of the quartz mercury arc. The arc lines used were isolated by passing the light through a Hilger quartz monochromator and using an Eastman filter which cut out all stray light of higher frequencies. The great amount of long wave-length energy radiated from a glowing tungsten filament made it easily possible to measure stopping potentials for light of wave-lengths up to 8000A with surfaces sensitized by means of dielectrics. This light was passed through a monochromator and a light filter cutting out higher frequencies, and the stopping potentials determined. Corrections for slit width were made before plotting the results. The stopping potentials were then redetermined using a

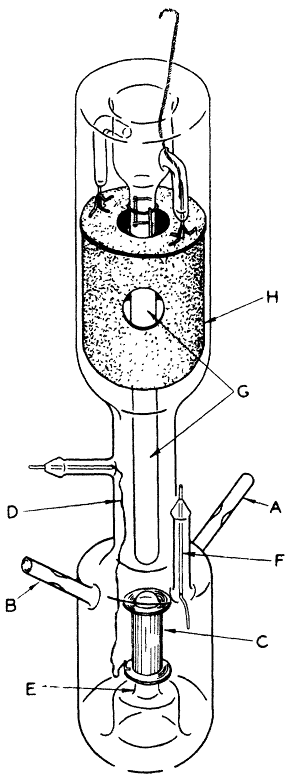

Fig. 37. Specially designed photoelectric cell for the study of stopping potentials. *A*—Tubular connection to evacuating system and entrance for sodium. *B*—Tube leading to side arm containing sulphur. *C*—Cathode of cell on which sodium is deposited. *D*—Phosphor bronze ribbon connecting cathode with external electrode. *E*—Glass stem supporting cathode while it is coated and sensitized and in which CO_2 snow was packed. *F*—Electrode forming electrical contact with coating of sodium used as temporary anode. *G*—Tube down which the sensitized cathode slides after it is sensitized and in which was kept a heating coil during the coating process. *H*—Insensitive anode to which the electrons were emitted after the tube was made.

monochromator of different dispersion. The results obtained with the different instruments checked perfectly.

Both for pure sodium and sodium treated with sulphur vapor and air the curves obtained were straight lines of slope *h*, as shown in Fig. 38. The value of *h* obtained from the pure sodium cannot be considered so accurate as that obtained from the sensitized sodium surface because of the few points on the curve and the narrow spectral band to which they are confined. However, even the value $h = 6.6 \times 10^{-27}$ can be considered a fair check of this important constant.

The curve taken after sensitizing the sodium as described earlier in this paper was very carefully determined with wave-lengths of light varying from 3500A to 8000A°, and, the value of *h* ($= 6.541 \times 10^{-27}$) can be considered accurate to at least three significant figures. Perhaps this is the first time that stopping potentials for light of wave-lengths longer than λ5461A have been used in the determination of the value of *h*.

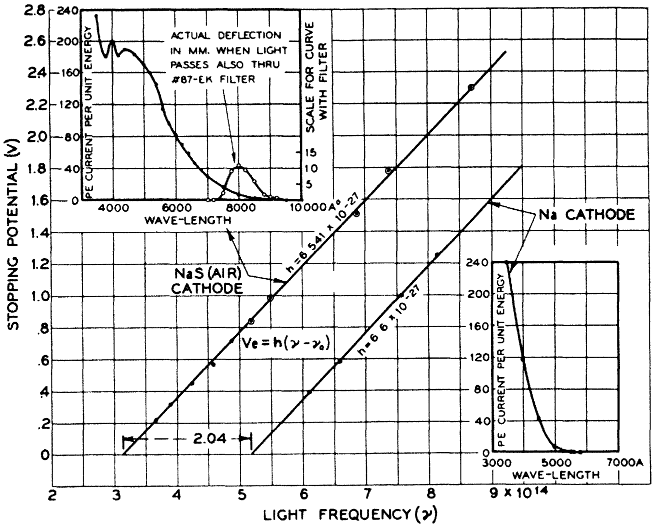

Fig. 38. Stopping potentials versus light frequencies for a sodium cathode before and after sensitizing it with sulphur and air treatments. The spectral response curves for both conditions are shown in the insets.

We never observed any line of slope 2*h*. This excludes the idea of a transfer of energy to a normal molecule from two exciting quanta.

When we plot true stopping potentials (measured in the manner just described) against light frequency for pure sodium and treated sodium as is done in Fig. 38, we obtain two parallel lines displaced from one another by the frequency shift δ corresponding to 1.47μ which has already been emphasized. When we plot *apparent stopping potentials* as read by the voltmeter, the two lines fall on one another (Fig. 39). This signifies that the surface work-function of the treated surface has been diminished and the contact potential increased by the amount corresponding in volts to δ. The electrons initially received the energy $h\nu$ from the quanta, but lose less of it in getting out through the surface, so that in effect their kinetic energy after escape is greater by $h\delta$ than it was with the pure sodium. By the Raman shift theory their kinetic energy would also have been greater by $h\delta$ after the treatment of the surface; but then the surface work function and the contact potential would have remained the same, and the apparent stopping potentials would have been shifted by δ.

To put the foregoing statements into algebraic form we may write the V of equation (2) as the sum of the P.D. registered by the voltmeter, say V_0, and the contact potential difference K:

$$(V_0 + K)e = h(\nu - \nu_0) = \tfrac{1}{2}mv^2. \tag{3}$$

Now, it is generally agreed by all investigators that when the anode is preserved unchanged, and different surfaces are used as cathodes, the stopping potential for a given wave-length of light is the same for all. Therefore, if we use primes to denote the values of V_0 and K for treated as distinguished from untreated sodium, we have,

$$(V_0' + K') - (V_0 + K) = h/e(\nu_0 - \nu_0'). \tag{4}$$

If the light frequency remains unchanged, $V_0' - V_0 = 0$, and

$$K' - K = h/e(\nu_0 - \nu_0'). \tag{5}$$

If, however, the incident light frequency is modulated, and the surface work function remains unchanged, $V_0' - V_0$ would not be zero and Eq. (7) would not explain the facts. Here was a criterion for deciding whether or not the light was modulated.

The stopping potential curves shown in Fig. 39 all refer to the same cell, one of the type shown in Fig. 37. It will be seen that the apparent stopping potentials for a given wave-length of incident light are the same before introduction of the dielectric as after.[33] The increased velocity of emission of the electrons after treatment with sulphur and air was due to a reduction of the work-function of approximately 0.8 volt which was the contact difference of potential between pure sodium and the sodium treated with the dielectric. For this particular case, then, Einstein's equation might be extended to read:

$$K' - K = \frac{h}{e}(\nu_0 - \nu_0') = \frac{h}{e}\,\frac{c}{1.47\mu}\,\cdot \tag{6}$$

Here is ample evidence that the light frequencies incident on the surface are not modulated.

Referring again to Fig. 39 attention is called to the way in which all plots of the light frequency versus apparent stopping-potentials, (voltages

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[33] Actually, the cathode voltage at which the current became zero was 0.5 volt more positive before admitting the dielectric than after, but this was due to the fact that the sulphur vapor and air which entered the cell had made the anode more electronegative as well as the cathode more electropositive.

at which no electrons reach the anode) fall on the same straight line which intersects the effective zero voltages at frequencies corresponding to the long wave limits of the respective cathodes. Failure of the voltage-current curves to break exactly at the effective zero is due to the fact that the anode did not enclose the cathode completely as explained above. A slight positive voltage had to be supplied to the anode before it gathered all of the emitted electrons. However, the separation of the voltages at which the currents saturate, designated by (b) and (d) and the separation of the effective zeros (a) and (c) are practically identical, and the relationship between the difference in contact potential and the shift in the long wave limit is graphically shown in the figure.

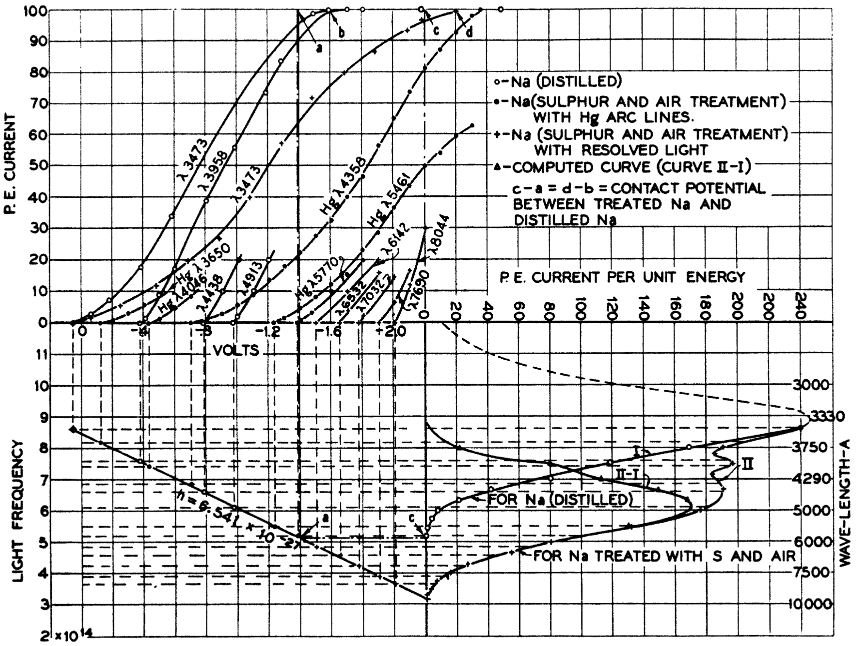

Fig. 39. Showing relationship between stopping potentials, light frequencies and photoelectric current per unit energy; and between contact potentials and long wave limits or work functions.

Now, contact difference of potential is generally considered a measure of the relative densities of free, conduction electrons existent in a substance. In other words, if when two conductors are electrically connected, electrons flow from one to the other, the one from which they flow is said to have a positive contact difference of potential with respect to the other. If, however, the photoelectron be considered to be the valence electron, in the atom, as has been done in this discussion, and the shift in the long wave limit be a measure of the decrease in its resonance frequency and correlate with the vibration-rotation frequencies of the surface molecules, it would appear that contact difference of potential was a property not alone of surfaces but of molecules and, as such, a measure of the relative number of available valence electrons under excitation of light, or the relative ease with which these loosely bound electrons can be liberated by light.

I. GENERALIZATION OF THE LINDEMANN FORMULA

In 1911 F. A. Lindemann[34] derived, from each of two very simple models, the following formula for a natural frequency ν which he proceeded to identify with the frequency of the selective photoelectric maximum:

$$2\pi\nu = (ne^2/mr^3)^{1/2} \quad (e,\ m \text{ charge and mass of electron}). \tag{7}$$

This is the frequency of an electron revolving in a circular orbit of radius r (or an elliptical orbit of major axis r) about a stationary charge of magnitude $+ne$. It is also the natural frequency of vibration of a system composed of two interpenetrating spheres of continuously-distributed positive and negative charge, having radii r, and total charges $\pm ne$ and $\pm e$ respectively.

Putting n equal to unity, and putting for r the radii of the atoms of the various alkali metals (obtained from their atomic volumes in the solid state) Lindemann obtained numerical values very close to the frequencies of the chief selective maxima of these metals as then known and subsequently checked (Pohl and Pringsheim, Braun,[35] Seiler,[36] and others). See Fig. 29. His values and the experimental ones, converted into wave-lengths, are shown in Table IV.

TABLE IV. *Specific wave-length of selective photoelectric effect.*

Metal	By Lindemann Formula	Observed
Cs	5500	5100
Rb	4900	4800
K	4380	4350
Na	3180	3400
Li	2360	2800

Subsequently Gross[37] showed that additional maxima observed by some workers for certain of the alkali metals fall at frequencies ν agreeing well with the formula

$$2\pi\nu = (ne^2/mr^3)^{1/2}$$

provided proper integer values be assigned to n.

Some of these agreements are so noteworthy, that it seems worth while to use the Lindemann model, primitive though it may appear in the light of recent theory. Now the choice of the value unity for n, which Lindemann

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[34] F. A. Lindemann Verh. d. D. Phys. Ges. **13**, 482 (1911). Verh. d. D. Phys. Ges. **13**, 1107 (1911).

[35] Braun, "Die Photoelektrischen Wirkungen der Alkali Metalle in Homogenen Licht," Boun 1906.

[36] E. F. Seiler, reference 5.

[37] F. Gross, reference 3.

made, corresponds to an electron revolving around a singly-charged ion—the sort of ion one would expect from a monovalent substance, such as the alkali metals are. Such values as 2, 3, ... for n would correspond to an electron revolving around a doubly-, triply-, ... charged ion, such as a di-, tri- .... valent substance would have. We might then say that in some atom-groups the alkali metals are divalent or trivalent, and that these are responsible for the maxima of higher frequencies which Gross considered.

Now in our experiments, we have checked several of the maxima to which the original Lindemann formula and the formula with Gross' modifications apply; and we have also observed maxima of lower frequency—those to which this paper is chiefly devoted—many of which are located at frequencies given by the Lindemann formula, provided that simple fractional values are assigned to the factor n.

Continuing with the model, we might say that such values of n are associated with atoms of valency $\frac{2}{3}$, $\frac{1}{2}$, and the like. To think of an electron revolving around an ion with net charge $+2e/3$ seems strange at first; but it is quite conceivable that the forces exerted on the electron by the other surrounding atoms might have the same net effect. We propose therefore to designate even the fractional values of n as "valencies".[37a]

Our data, together with those of the observers already quoted, are listed in Tables V, VI and VII, being classified according to the metals involved. The second column of each table gives the various values assigned to n; the third the corresponding wave-lengths, derived from the frequency computed by the generalized Lindemann formula; the fourth, the wave-lengths of the observed maxima; the fifth, the authorities. In the first column, we give the formulae for oxides in which the metal in question displays these valencies.

Now it is an important fact that most of these oxides are known to exist.[38]

TABLE V. *Lindemann formula* $\nu_{\max} = (1/2\pi)(ne^2/mr^3)^{1/2}$.

Metal and its oxides	Valence of metal	$\lambda_{\max}$ (Computed)	$\lambda_{\max}$ (Observed)	Observer
Na	1.	3170	3400	Pohl and Pringsheim
Na_4O	0.5	4500	4700	Self (Figs. 14, 29, 42, 43.)
Na_3O	0.67	3900	4000	Self (Figs. 14, 42, 43.)
Na_2O	1.	3170	<3500	Self
Na_2O_2	2.	2250	2270	Richardson and Compton[6] (On impure Na)
(Na_2O_3)*	3.	1820		

* Probably solid solutions or mixtures of R_2O_2 and R_2O_4.

Returning to the data reported in this paper, an attempt will now be made to interpret them in a way suggested by the Lindemann theory. Among

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[37a] Fractional valences are recognized by the chemists by such formulae as $CdCl_2$, 2.5 H_2O, $CdSO_4$, 2.66 H_2O (I.C.T. Vol. 1, p. 120).

[38] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 2, p. 485, Longmans, Green and Co. Ltd., London.

the oxides of sodium are listed Na_4O, Na_3O,[39] Na_2O and Na_2O_2, showing valencies for sodium ranging from 0.5 to 2. Since the likely presence of traces of water vapor in all the dielectrics introduced onto the alkali metals has been admitted and since atmospheric air was admitted in some cases, it may well be that some oxide is formed on the cathode surface; and this may have been a suboxide. (The formation of the higher oxides should result in increasing the response to shorter wave-lengths.) As evidence that it actually was a suboxide, I cite experiments which showed that the cells were red-sensitive only when very small amounts of the dielectrics were used. If a certain critical amount was exceeded the response to red decreased greatly, and soon entirely disappeared. If, however at this stage a point

TABLE VI. *Lindemann formula* $\nu_{\max}=(1/2\pi)(ne^2/mr^3)^{1/2}$.

Metal and its oxides	Valence of metal	$\lambda_{\max}$ (Computed)	$\lambda_{\max}$ (Observed)	Observer
K	1.	4380	4350	Pohl and Pringsheim
K_4O	0.5	6200	6200	Self (Fig. 34)
K_2O	1.	4380	4200	Self (Fig. 34)
K_2O_2	2.	3100	3130	Wiedmann
(K_2O_3)*	3.	2520		
K_2O_4	4.	2240		
K_8O_5	1.25	3920	4000 to 3500	Self (Fig. 34)
K_6O_4 †	1.33	3800		
K_4O_3	1.5	3580		

* Probably solid solutions or mixtures of R_2O_2 and R_2O_4.
† Probably aggregates or mixtures of R_2O and R_2O_2.

TABLE VII. *Lindemann formula* $\nu_{\max}=(1/2\pi)(ne^2/mr^3)^{1/2}$.

Metal and its oxides	Valence of metal	$\lambda_{\max}$ (Computed)	$\lambda_{\max}$ (Observed)	Observer
Cs	1.	5500	5100 5400	Braun Miss Seiler
Cs_7O	0.29	10200		
Cs_4O	0.5	7800	7700	Self (Fig. 8(a))
Cs_7O_2	0.57	7300	7200	Self (Fig. 8(b))
Cs_3O	0.67	6700		
Cs_2O	1.	5500	5500	Self (Fig. 8 (c))
Cs_8O_5	1.25	4900		
Cs_6O_4 †	1.33	4750		
Cs_4O_3	1.5	4400		
Cs_2O_2	2.	3900	3900	Richardson and Compton[6]
(Cs_2O_3)*	3.	3160		
Cs_2O_4	4.	2760	2500	Richardson and Compton[6] (On impure Cs)

* Probably solid solutions or mixtures of R_2O_2 and R_2O_4.
† Probably aggregates or mixtures of R_2O and R_2O_2.

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[39] R. de Foicrand, Compt. Rend. **127,** 364, 514 (1898).

near the cell window was heated, a vapor of sodium plus some of the dielectric was created in the cell. This lent itself to the formation of a subvalent compound on the surface and the characteristic response to light of long wavelengths was again in evidence. Moreover, the general appearance of the cathode of sodium cells so treated was exactly that of sodium suboxide, viz. a grey, porous surface crust.

Suboxides of potassium[40] and caesium[41] are also known, but they are more difficult to prepare and apparently are only obtained by limiting the amount of oxygen first coming in contact with the metal. Really this is to be expected for it is impossible to prepare oxygen sufficiently dry that it will not react with either potassium or caesium, but sodium can be distilled in dry oxygen without reaction. In the case of caesium, the suboxides are only formed by limiting the amount of oxygen present and holding the temperature at a certain value. Naturally, then, it would be expected that sodium-suboxide photoelectric cells could be made with less difficulty than potassium or caesium suboxide cells. However, by flashing hydrogen on thin potassium films deposited on oxidized copper plates in vacuum, very much as Campbell[42] has reported, a compound which apparently was potassium suboxide, was prepared. Also by proper control of the temperature, as caesium vapor came in contact with an oxidized silver plate in vacuum, caesium suboxide was formed. Each of these compounds produced a new and pronounced maximum in the spectral response curves, the former at 6200A and the latter at about 7700A. (See Figs. 32 and 7.)

There is no reason to assume, however, that such subvalent compounds are limited to the oxides. The main and limiting requirement for red sensitivity is undoubtedly the subvalent condition of the atoms in the molecules, and possibly these may be subhalides, subsulphides, or some other subvalent salts. However, not many such compounds are known; and water vapor was in all probability always present in the small amounts likely to form suboxides. The broadening of these maxima in cases when certain dyes or dielectrics were used (Figs. 12, 25) was probably due to intense absorption of these complex compounds on the long wave side of this maximum.

The work of Dima[43] on the oxides of manganese and various compounds of other metals suggests a similar theory; for using unresolved light, he found that the lower the valency of the metal in the compounds, the more photosensitive the compound. This may have been due to the shift of the maximum towards the red.

It is practically impossible to prepare a suboxide of a metal without at the same time forming some higher oxides as well. These should correspond to integer values of n in Lindemann's formula; and maxima explainable in this way have actually been observed. As in the case of the maximum for $n=1$

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[40] J. J. Berzelius, Lehrbuch der Chemie, Dresden **1,** 749 (1825).

[41] E. Rengade, Compt. Rend. **148,** 1199 (1909).

[42] N. R. Campbell, Phil. Mag. **6,** 633 (1928).

[43] Dima, Compt. Rend **176,** 1366 (1913); **177**; 590 (1913).

shown by multiply distilled sodium, the additional maxima for treated sodium surfaces also generally fall at slightly greater wave-lengths than the computed values, (Table V). However, the second selective maximum observed in the ultraviolet by Richardson and Compton for sodium fits closely the maximum to be expected if $n=2$, the valence of Na in Na_2O_2. The shift of the long wave limit to greater values suggests the presence of the suboxide ($n=0.5$) in small quantities. Since their experimental conditions precluded the possibility of thoroughly eliminating moisture from the glass walls, the likelihood of these compounds being present must be admitted.

The last three oxides listed in the potassium group (Table VI) may have been responsible for the apparent shift of the regular selective maximum for that metal to shorter wave-lengths as quite generally observed after treatment with the dielectrics, (Figs. 5, 23). Moreover, for $n=2$ (the valence of K in K_2O_2) Lindemann's formula gives a maximum at almost exactly the same wave-length as that attributed to oxygen on potassium by Wiedmann.

The difficulties in preparing pure, silvery caesium in bulk form may explain why most investigators seeking to establish the presence of a selective maximum at $\lambda 5500A$ ($n=1$ in the Lindemann formula) for caesium, found a greater peak in the ultraviolet. For, even after multiply distilling caesium in vacuum, it usually appears slightly golden in color as if containing some oxides. If the valence of Cs in these oxides is greater than unity ($n>1$) the selective maxima should fall in the ultraviolet,as observed. As a matter of fact, experiments show that by introducing caesium onto an oxidized plate under proper temperature conditions, the regular selective maximum ($n=1$) can be made to disappear almost entirely, as shown in Fig. 7, indicating that practically all free caesium had disappeared. At the same time the maxima due to the suboxides ($n<1$) and peroxides ($n>1$) become very pronounced.

In the foregoing computations the value of the atomic radius r was left unchanged as n was modified. The alkali metal atom in the molecule was considered as an isolated atom of normal dimensions but with a different force-constant.

J. COMPARISON OF AFORE-MENTIONED HYPOTHESES

Two seemingly different and unrelated theories have been advanced to explain the displaced selective maximum. In the first one it was assumed that there is hydrogen present, a condition not unlikely since sodium and potassium absorb great quantities of this gas without any change in their metallic appearance, much as does palladium.[44] It is further assumed that addition of some such dielectric as oxygen or nitrogen results in the appearance of characteristic vibration-rotation frequencies which were apparently subtracted from the resonance frequency of the electron in the alkali metal atom. The other theory is based on the Lindemann equation, and accounts for the reduced resonance frequency as a consequence of a decreased binding

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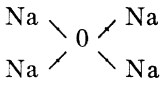
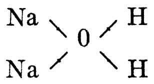
[44] P. Hautefeuille and L. Troost, Ann. Chem. Phys. (5), **2,** 273 (1874), Compt. Rend. **78,** 809 (1874).

force on the electron correlated with a change in the valence of the alkali metals in the molecules of the compound formed on the cathode, the atoms in a subvalent condition responding to light of longer wave-lengths.

Until more is known concerning valence and molecular structure, attempts to correlate the two theories would be outright conjecture. It may be that the reason the two theories appear to explain the same phenomena is that they are both built around similar structures. For example, the very unusual molecule Na_4O may be structurally written (for want of a better formula)



On the other hand, if hydrogen is assumed present with the alkali metals the introduction of oxygen (say) into a photoelectric cell and subsequent treatment, as described above, might result in the formation of molecules which may be written:



In this connection, it is significant that dry oxygen will not react with sodium. Now, the valence of the sodium atom in each of these compounds is identical, and yet the latter is shown to contain the atoms giving rise to the spectrum of water vapor. The valence of the sodium atoms being similarly reduced in each case, the resonance frequency of the valence electron would be correspondingly decreased and the response to long wave light increased.

Either theory may be made to account for the observation that for small ratios of oxygen atoms (say) to alkali metal atoms in a molecule, the response to red light becomes greater. This would be expected by the first theory, for when the atoms are attentuated, higher vibration-rotation frequencies become sharper, as pointed out previously for the case of water of crystallization.[45] It would also be expected by the second theory, for the valence of the metal and consequently the binding force on the electron would correspondingly be lessened.

K. IRREGULARITIES IN VOLTAGE-CURRENT CURVES EXPLAINED

The fact that higher voltages are required to bring about current-saturation when the surfaces are irradiated with light of large wave-lengths can be easily explained by a comparison of the contact potentials of the materials comprising the cathodes of red-sensitive cells. Experiment showed (Fig. 39) that the complex surface formed when the dielectrics were introduced onto an alkali metal cathode was electropositive with respect to the metal by as much as 0.8 volt, and since, within distances comparable to molecular diameters, both free atoms and these complex molecules were existing on the surface, electrons released from the molecules by long wave light would

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[45] W. W. Coblentz, reference 19.

encounter strong opposing fields and their escape would be impeded. They would be pulled to the anode only when sufficient voltage was applied to offset these local surface fields. On the other hand, electrons released by light of shorter wave-lengths come primarily from the free atoms and since these are electronegative with respect to the molecules on the surface, the electrons encounter a helping rather than an impeding force. Consequently, the photoelectric current will saturate at lower voltages for blue light than for red light.

The phenomena, shown in Figs. 2, 3 and 28 and which might be called supersaturation, may be explained by the shape of the elements of the tube. To understand better why more electrons should reach the anode at low voltages than at high, the history of the cell will be reviewed. The first step after evacuation of the bulb was the coating of the entire inner walls with potassium or sodium. Next, by applying a fine point flame momentarily on the face of the bulb, the metal was caused to recede and form an opening through which light could enter the cell. But without thorough heating, the glass could not be made perfectly non-conducting; and on account of the low melting points of the alkali metals, prolonged heating of the "window" would have ruined the entire coating of the cell. Even if it were temporarily cleaned of all potassium, the high vapor pressure of the alkali metal produced by the heat of the flame would have deposited metal enough on the window to make it conducting afterward.

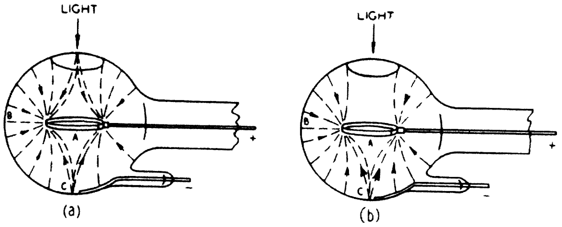

Fig. 40. Diagrams indicating the geometry of the electric fields within photoelectric cells having closed ring anodes (a) before treatment with dielectrics and (b) after such treatment.

Now, the general shape of the electric field set up by an applied polarizing voltage within such a cell might be represented by the direction lines of diagram (a) Fig. 40. It is at once evident that the effect of increasing the polarizing voltage would be that of increasing the number of electrons reaching the anode up to complete saturation. This would result in a normal voltage-current relation. When, however, the conducting film on the glass window was destroyed by some active gas or dielectric, or by repeated heating afterward, the shape of the polarizing field changed to that illustrated by the directional lines of diagram (b). In effect the field between the window and the closed ring or anode was wiped out. From the point *C* the field spread radially toward the plane of ring *A*. For such a field there is a critical voltage at which the greatest number of emitted electrons arrive at a collector located at some angle to the normal from an illuminated spot. These voltages have been computed for a similar case and published by Fry and Ives[46] and their computations experimentally verified by Ives, Olpin and Johnsrud[47] for central cathode photoelectric cells. The striking similarity of their curves and the voltage-current curves shown in Fig. 28, for illumination at back and side of cells treated with dielectrics, is illustrated in Fig. 41. It might also be that the greater energies of emission after treatment with the dielectric tended to augment this condition.

Apparently then, the closed ring used for the anode of these cells was responsible for these peculiarities in the voltage-current relation. Data obtained from cells having different shaped anodes, such as straight wires or grids, failed to show these peaks at low voltages. Finally a cell was made having a closed ring anode which could be rotated and set with its plane perpendicular to or parallel to the illuminated spot on the cell wall. Whenever, the plane of the ring was parallel to the back of the cell on which the light was falling, the peaks at low voltages appeared and whenever the ring was turned through 90° these maxima disappeared.

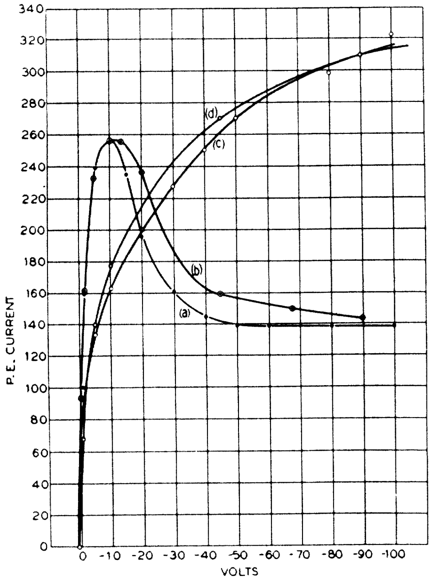

Fig. 41. Comparison of voltage-current curves obtained with photoelectric cells having closed ring electrodes as shown in Fig. 40(b) and voltage-current curves observed with anodes fixed at given angles to the normal to the cathode for cells having radial fields, as described by Ives, Olpin and Johnsrud.[47] a—Curve 4 of Fig. 28. Light incident at *C* (Fig. 40) b—Curve for a cell with a radial field when the collecting segment was located at 10° to the normal from the cathode. c—Curve 6 of Fig. 28. Light incident at B (Fig. 40). d—Curve for a cell with radial field when the collecting segment was located at 10° to the normal from the cathode.

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[46] T. C. Fry and H. E. Ives, Phys. Rev. **32,** 44 (1928).

[47] H. E. Ives, A. R. Olpin, A. L. Johnsrud, Phys. Rev. **32,** 57 (1928).

L. CONSIDERATIONS IN THE REALM OF PHOTOGRAPHY FLUORESCENCE AND LIGHT ABSORPTION

While there is not space for more extensive discussions, it seems important to call attention to apparently analogous phenomena in the fields of photography, light absorption and fluorescence. It certainly seems more than a coincidence that photographic plates and photoelectric cells can be sensitized to red and infrared light by such strikingly similar methods. The presence of traces of sulphur in the gelatines obtained from some sources has been given by investigators at the Eastman Research Laboratories[48] as an explanation for their high sensitivity to light. Certainly these experiments, together with those wherein photographic plates are sensitized to red and infrared light by means of organic dyes, suggest a close relationship between photographic and photoelectric phenomena.

Saha[49] and others have already advanced theories in which fluorescence with change of wave-length is attributed to modulation of the exciting light. In general, however, his conclusions have not been enthusiastically received, many unexplainable observations standing in the way of such a theory. Certainly, however, it should not be dismissed without further consideration. Such results as Wood and Kinsey[50] reported wherein the *D* lines of sodium were excited by radiation in the region of 5100–5250A when the sodium vapor was mixed with low pressures of hydrogen, nitrogen or air, seem significant, indeed, since the wave-length region of the exciting radiation here coincides with that of the new photoelectric maximum in the spectral response curves for sodium cathodes treated with air, and the photoelectric threshold for pure sodium atoms coincides with the *D* lines.[51]

Many other closely analogous phenomena might be mentioned here; such, for instance, as the fact that the absorption lines of an absorbing medium are noticeably shifted to longer wave-lengths when the absorbing medium is dissolved in a dielectric.[52] But these are beyond the scope of this paper.

ACKNOWLEDGMENT

To Mr. G. R. Stilwell for invaluable contributions to the technique and art involved in the manufacture of the cells described above, to Dr. Herbert E. Ives for careful consideration of problems encountered in this investigation and for helpful suggestions, and to Dr. K. K. Darrow and Dr. Homer H. Lowry for constructive study of this manuscript, the author expresses his heartiest appreciation.

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[48] A. P. H. Trivelli, Frank. Inst. J. **205,** 111 (1928).

[49] M. N. Saha, D. S. Kothari, G. R. Toshniwal, Nature **122,** 398 (1928).

[50] R. W. Wood and E. L. Kinsey, Phys. Rev. **31,** 5, 793 (1928).

[51] H.E. Ives and A. R. Olpin, Phys. Rev. **34,** 117 (1929).

[52] Aschkinass and Schaeffer, Ann. d. Physik **5,** 489 (1901).

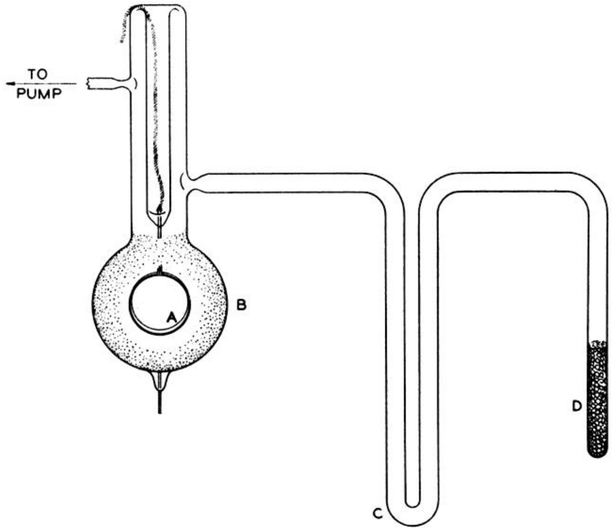

Fig. 1. Experimental type photoelectric cell. *A*-Ring-shaped anode. *B*-Bulb coated on inside with alkali metal to form cathode. *C*-Liquid air trap. *D*-Side arm containing dielectric.

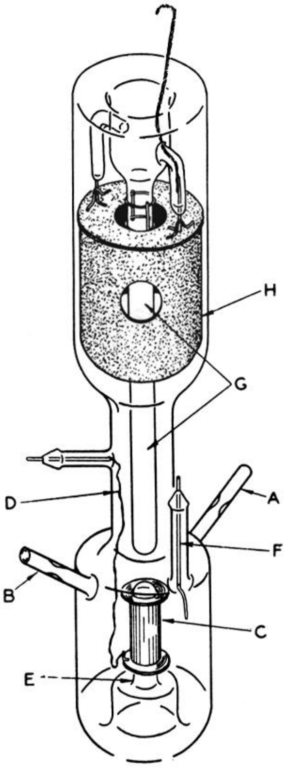

Fig. 37. Specially designed photoelectric cell for the study of stopping potentials. *A*—Tubular connection to evacuating system and entrance for sodium. *B*—Tube leading to side arm containing sulphur. *C*—Cathode of cell on which sodium is deposited. *D*—Phosphor bronze ribbon connecting cathode with external electrode. *E*—Glass stem supporting cathode while it is coated and sensitized and in which CO_2 snow was packed. *F*—Electrode forming electrical contact with coating of sodium used as temporary anode. *G*—Tube down which the sensitized cathode slides after it is sensitized and in which was kept a heating coil during the coating process. *H*—Insensitive anode to which the electrons were emitted after the tube was made.